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Coenzyme B_{12} model studies : Equilibria of axial ligation of alkyl (aquo) cobaloximes with bilogically important ligands

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Abstract

Equillibria of the reaction of alkyl(aquo)cobaloxime (alkyl = $BrCH_2$,CH_3, or C_2H_5) with imidazole, substituted imidazoles, histamine, histidine, glycine and ethyl glycine ester were studied as a function of pH at 25°C, 1.0M ionic strength(KCl) by UV-VIS spectrophotometry. Comparison of equilibrium constants with respect to ligand are in the order $K_{1\text{-Mim}} > K_{\text{Im}} > K_{\text{Hisdn}} > K_{\text{Hiamn}} > K_{\text{Gly}} > K_{\text{Glyest}} > K_{2\text{-Mim}} > K_{1,2\text{-Dmim}} > K_{2\text{-Etim}}$. The equilibrium constants with respect to alkyl group (R) are in the order $BrCH_2 > CH_3 > C_2H_5$. The equilibrium constants are correlated to the softness and ability to form dπ-pπ back bonding.

(**Keywords** : alkyl cobaloximes/dimethylglyoxime/equilibrium constants/imidazole/substituted imidazoles/histamine/histidine/glycine/glycine ester)

Introduction

Model complexes for vitamin B_{12} such as alkyl(aquo)cobaloximes have played an important role in understanding the behaviour of the ligand substitution reactions of vitamin B_{12} and the role of the Co-C bond in the coenzyme vitamin B_{12}[1,2]. Imidazole is a typical representative of a large group of heterocyclic nitrogen donor atom ligands. Imidazole and its derivatives are components of a variety of biologically important molecules, where they play a role as ligands[3-5]. Imidazole normally coordinates the metal ions through its pyridine nitrogen, although it is potentially an ambidentate ligand, which can also bind *via* the pyrrole nitrogen[6]. The understanding of the chemistry of cobalamins requires extensive studies of several types of model systems.

The ligand substitution reaction of trans $[Co(en)_2Me(H_2O)]^{2+}$ and trans $[Co(en)_2Me(NH_3)]^{2+}$ were studied for CN^-, SCN^-, N^-_3 and NH_3 as entering nucleophiles[7]. Eldik *et al.*[8] studied formation constants for the reaction of $[Co(Me_6tren)H_2O]^{2+}$ with different pyridine – imidzoles and the kinetics of these reactions was studied as a function of ligand concentration. Equilibria and kinetics of the reaction of alkyl(aquo)cobaloxime with aromatic and aliphatic N-donor ligands were studied[9-12] as a function of pH and ligand concentration. A series of trans azido(ligand)cobaloximes were studied by Reddy and Satyanarayana[13]. Eldik *et al.*[14] studied the reaction of cyanide with different alkylcobalamins (R = CF_3, CF_3CH_2, CH_3, CH_2Br) and found that the nature of the alkyl group has an influence on the thermodynamic equilibrium constants, kinetics and mechanism of the substitution reactions of the axial ligand trans to the alkyl group.

Materials and Method

Imidazoles, substituted imidazoles, histamine (histamine dihdrochloride), histidine (histidine monohydrochloride), glycine and ethyl glycine ester were obtained from Sigma and were used without further purification. KCl, HFLC grade methanol, acetic acid, HCl, phosphoric acid, formic acid were

obtained from Fluka. Di potassium hydrogen phosphate, potassium dihydrogen phosphate, potassium phosphate, Tris, sodium acetate, potassium hydroxide were obtained from Acros. Double distilled, deionized water was used throughout.

To maintain desired pH appropriate buffer of 0.2M concentrations were used. Alkyl(aquo) cobaloximes were prepared by the procedure of Brown[15]. All manipulations were performed under minimal illuminations due to photolability of organo cobalt bond[16]. These alkyl(aquo)cobaloximes are photo labile, particularly in solution. Soluble in alcohols and DMSO, less so in chloroform or water and virtually insoluble in ether and hydrocarbon solvents.

UV and visible spectra were recorded on a Hitachi U-3410 spectrophotometer, the sample compartment of which is provided with a thermostat and the concentrations of bromomethyl(aquo) cobaloximes (0.00125 M) was fixed at 436nm,while for methyl (aquo) cobaloxime and ethyl (aquo) cobaloxime 0.0006 M concentration was fixed at 442nm and 451nm respectively.

Equilibrium measurements : Values for the pKa of the conjugate acid of ligands were obtained by potentiometric titration at 25±0.1°C. Values of pKa's were obtained by algebraic method[17] from the eqn. (1).

$$Ka = [L^-]\ [H^+]\ /\ [HL] \quad (1)$$

In a 3 ml cuvette solutions containing $RCo(DH)_2(OH_2)$ an appropriate buffer (0.2 M) to maintain pH, KCl to maintain ionic strength (1.0 M) and varying concentrations of ligand were taken in a cell maintained at 25 ± 0.1°C. Solutions were allowed to temperature – equilibrate in the spectrophotometer cell block for at least 15min. Final absorbance readings were taken after equilibrium was established as indicated by the time independence of the readings.

$$K_{app} = \frac{[RCo(DH)_2L]}{[RCo(DH)_2H_2O]\ [L]} \quad (2)$$

$$\Delta A = \Delta A_{max} - \{1/K_{app}(\Delta A/[L]_f)\} \quad (3)$$

where ΔA is the difference in absorbance between solutions containing cobaloxime and added ligand and solutions containing only cobaloxime at the same concentration, ΔA_{max} is the maximum absorbance change thus obtained at high $[L]$, and $[L]_f$ is free ligand concentration. The data were analysed by a least-squares fit to the eqn. (3)

$$[L]_f = [L]_{tot} - (C_T \Delta A\ /\ \Delta A_{max}) \quad (4)$$

$[L]_f$ is calculated from eqn. (4) using measured value of ΔA_{max}, where $[L]_{tot}$ is the total concentration of added ligand and C_T is the total concentration of cobaloxime. Values of K_{app} were obtained from the least-squares fit of eqn. (3) i.e., the plot of ΔA *vs.* $\Delta A / [L]_f$. And the slope is K_{app} the pH independent equilibrium constant (K_{eq}) is calculated from the relation

$$K_{eq} = K_{app}\ /\ \alpha_L.$$

where α_L is the fraction of the ligand present as free base (unprotonated) and is calculated from the eqn. (5).

$$\alpha_L = \frac{Ka}{(Ka + [H^+])} \quad (5)$$

Results and Discussion

The dependence of pH on the binding of ligand (imidazole) to the cobaloxime (ethyl(aquo)cobaloxime) is shown in Fig. 1. This shows as the pH is increased the apparent binding constant increased.
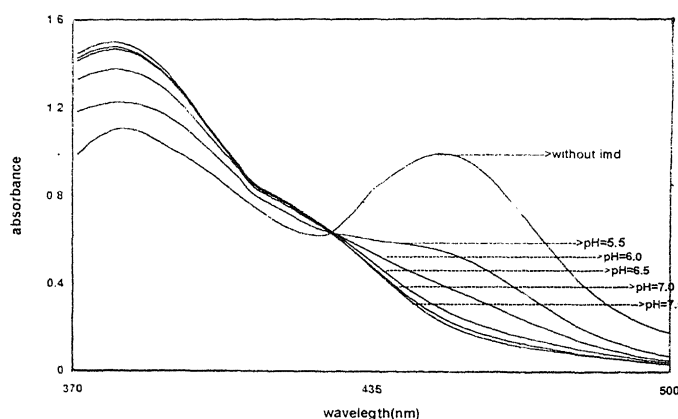
Fig. 1 - Effect of pH on the binding of $C_2H_5Co(DH)_2OH_2$ with 1.5×10^{-2} M imidazole at 25°C, isosbestic point = 425 nm.

The values of log K_{app} listed in Table 1 can be seen to increase markedly in the order R = $CH_3CH_2 < CH_3 < BrCH_2$. In all the three cases

the $K_{histidine}$ are greater than $K_{histamine}$, though histamine is slightly more basic than histidine. Histidine and histamine bind to Co(III), *via* N $\rightarrow$ Co σ donor as well as Co(III) $\rightarrow$ N π bond. An increase in basicity (in histamine)is associated with a decreased ability for histamine to function as a π acceptor. As π bonding becomes increasingly important the dependence of stability of $RCo(DH)_2L$ upon basicity are not observed. Histidine is less basic and better π acceptor than histamine, hence histidine forms more stable complexes than histamine.

The increase of stability with basicity can be well explained in case of only σ donor ligands (e.g. glycine and glycine ester). Glycine is more basic than glycine ester hence the stability order is [$RCo(DH)_2$ glycine] > [$RCo(DH)_2$ glycine ester]. An increase in basicity is associated with an increased ability for σ donation. Hence the greater dependence of $RCo(DH)_2L$ stability on ligand basicity for glycine and glycine ester are solely due to σ donor capacity. If we compare the pH dependent binding plots of glycine and glycine ester in both cases the K_{app} increases with increase in pH and after certain pH they become pH independent. Glycine shows pH dependence upto 10 pH latter becomes pH independent, whereas glycine ester binding will be pH dependent upto 8 pH and later it becomes pH independent (Fig. 2).
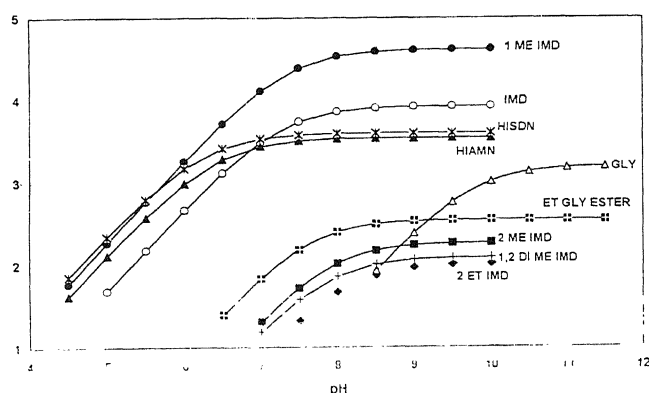
Fig. 2 - Effect of pH as the formation constants (log K_{app}) on the pH for the axial ligation of $CH_3Co(DH)_2OH_2$ by different ligands (L) at 25°C in aqueous solution, ionic strength 1.0 M (KCl).

The equilibrium constant for the ligation of $RCo(DH)_2\ OH_2$ by imidazole is dependent upon the pKa values of the conjugate acid of the ligands as the pH increases the apparent binding constant increases. The pH dependence of the apparent equilibrium constant for ligation K_{app} from pH 4.5 to 8.0 is consistent indicating Imd free base is the sole ligating species, as the pH is decreased the K_{app} decreased. The dependence of pH on the binding of imidazole to $RCo(DH)_2OH_2$ is shown in Fig. 2. This may be because of the competition of H^+ with Co(III) to bind with imidazole. Hence at lower pH most of the imidazole is protonated and not available for binding with cobalt. At higher pH imidazole (free base) available is maximum and binds to Co(III). So the K_{app} is larger at higher pH. Above 8.0 pH imidazole is completely free base and completely available for binding. Similar trends were observed with 1-Mim. In these two cases the pH dependent binding constants were measured from 4.0 pH to 10 pH to demonstrate the pH dependent and pH independent binding of these ligands to $RCo(DH)_2OH_2$. The order of stability among the cobaloxime is CH_2Br >CH_3 >C_2H_5.

Whereas in case of 2-Mim, 2-Etim and 1,2-Dmim the binding constants could not be measured below 7.0 pH, as they bind weakly to Co(III) of cobaloximes. Upto 8.0 or 8.5 pH their binding is pH dependent and above that pH their binding is pH independent. The order of stability with respect to imidazole is in the order 1-Mim > Im > 2-Mim > 1,2-Dmim > 2-Etim (Fig. 2). In case of 1-Mim and Im the stabilities increase with increasing basicity. Whereas from Imd to 1,2-Dmim though the basicity increases the stabilities decrease drastically. This may be attributed to the increase in steric hindrance due to the presence of methyl or ethyl group at C_2 of imidazole, since imidazole binds to Co(III) through N_3 atom. Similar trends were observed in the substitution reactions of $CH_3Co(DH)_2OH_2$ with $P(n\text{-}But)_3$ or pyridine[18]. Though $P(n\text{-}But)_3$ is more basic and greater π back bonding ability than pyridine, it reacts more slowly and forms less stable complexes than pyridine.

A soft or class b character has been assigned to $RCo(DH)_2OH_2$ cobaloximes[19,20], vitamin B_{12} and methyl cobaloximes[21] and is consistent with the observed greater ligand affinity of cyanide, imidazole, histidine or histamine than the hard glycine or glycine ester.

Table 1- Formation constants for the axial ligation of $RCo(DH)_2OH_2$ by various ligands, R= $BrCH_2$, CH_3, C_2H_5.

L	pH → R ↓	Log K_{app} at various pH for the axial ligation of $RCo(DH)_2OH_2$ by various ligands at 25° C.														
		4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	K_{eq}
Imidazole	$BrCH_2$	1.913	2.411	2.906	3.390	3.841	4.217	4.464	4.585	4.632	4.647	4.653	4.654	---	---	---	47344
	CH_3	---	1.686	2.181	2.664	3.116	3.491	3.739	3.860	3.906	3.922	3.927	3.929	---	---	---	8512
	C_2H_5	---	1.417	1.912	2.395	2.847	3.222	3.470	3.591	3.637	3.653	3.658	3.660	---	---	---	4580
1 Methyl imidazole	$BrCH_2$	1.999	2.498	2.994	3.481	3.942	4.340	4.617	4.762	4.820	4.840	4.847	4.849	---	---	---	70856
	CH_3	1.773	2.271	2.767	3.254	3.716	4.113	4.391	4.535	4.593	4.614	4.620	4.622	---	---	---	42040
	C_2H_5	1.543	2.042	2.538	3.025	3.487	3.884	4.162	4.306	4.364	4.384	4.391	4.393	---	---	---	24806
2 Methyl imidazole	$BrCH_2$	---	---	---	---	---	1.503	1.911	2.204	2.363	2.428	2.451	2.458	---	---	---	290
	CH_3	---	---	---	---	---	1.315	1.723	2.016	2.175	2.240	2.263	2.270	---	---	---	188
	C_2H_5	---	---	---	---	---	1.082	1.490	1.783	1.942	2.007	2.030	2.037	---	---	---	110
2 Ethyl imidazole	$BrCH_2$	---	---	---	---	---	1.006	1.442	1.785	1.994	2.088	2.123	2.134	---	---	---	138
	CH_3	---	---	---	---	---	---	1.327	1.671	1.879	1.973	2.008	2.019	---	---	---	106
	C_2H_5	---	---	---	---	---	---	1.256	1.601	1.808	1.902	1.937	1.948	---	---	---	90
1,2 Dimethyl imidazole	$BrCH_2$	---	---	---	---	---	1.437	1.834	2.112	2.256	2.314	2.334	2.341	---	---	---	221
	CH_3	---	---	---	---	---	1.189	1.586	1.864	2.009	2.067	2.087	2.093	---	---	---	125
	C_2H_5	---	---	---	---	---	1.079	1.476	1.754	1.899	1.957	1.977	1.983	---	---	---	97
Histamine	$BrCH_2$	1.821	2.310	2.776	3.184	3.479	3.639	3.704	3.727	3.735	3.737	3.738	3.739	---	---	---	5480
	CH_3	1.624	2.112	2.579	2.987	3.282	3.441	3.507	3.530	3.537	3.540	3.541	3.542	---	---	---	3478
	C_2H_5	1.385	1.874	2.341	2.749	3.043	3.203	3.269	3.292	3.299	3.302	3.303	3.303	---	---	---	2010
Histidine	$BrCH_2$	2.099	2.583	3.083	3.407	3.651	3.770	3.816	3.831	3.836	3.838	3.839	3.839	---	---	---	6900
	CH_3	1.863	2.346	2.797	3.170	3.415	3.534	3.579	3.595	3.600	3.601	3.602	3.602	---	---	---	4004
	C_2H_5	1.619	2.102	2.552	2.926	3.170	3.289	3.335	3.350	3.355	3.357	3.358	3.358	---	---	---	2280
Glycine	$BrCH_2$	---	---	---	---	---	---	---	---	2.335	2.787	3.162	3.409	3.530	3.57	3.592	3979
	CH_3	---	---	---	---	---	---	---	---	1.936	2.388	2.763	3.010	3.131	3.17	3.193	1588
	C_2H_5	---	---	---	---	---	---	---	---	1.637	2.089	2.464	2.711	2.832	2.87	2.894	798
Ethyl glycine ester	$BrCH_2$	---	---	---	---	1.829	2.267	2.616	2.830	2.927	2.963	2.975	2.979	2.980	2.98	2.982	958
	CH_3	---	---	---	---	1.398	1.836	2.185	2.398	2.496	2.532	2.544	2.548	2.549	2.55	2.551	355
	C_2H_5	---	---	---	---	---	1.380	1.728	1.942	2.039	2.075	2.087	2.091	2.092	2.09	2.094	124

The concept of metal to ligand π bonding will explain both the order of strength of ligation and the reverse order for the dependence of ligation strength upon ligand basicity. The order of $RCo(DH)_2L$ stability is attributed to the ability of imidazoles or histidine or histamine to accept electrons into higher energy unfilled π^* antibonding orbitals[22]. Whereas primary amine (glycine or glycine ester) cannot accept electrons in either fashion. This ligand stability order is the same as the order previously established for the trans direction of substituents into the square-planar complexes of Pt[23] and for the stabilization of low valent states of numerous transition metals[24], processes which have been related to the π - accepting ability of the ligands. The reverse order for the dependence of $RCo(DH)_2L$ stability on ligand basicity between the two series of ligands (imidazoles and amines, glycine or glycine ester) is not unexpected based on the following considerations.

1. An increase in basicity is associated with an increased ability for σ donation for example glycine forms more stable complexes than glycine ester, since glycine is more basic (pKa 9.74) than glycine ester (pKa 7.62)

2. An increase in basicity is associated with a decreased ability for the imidazole ligands and CN^- to function as π acceptors (here π bonding becomes increasingly important, progressively lesser dependencies of $RCo(DH)_2L$ stability upon ligand basicity are observed).

For CN^-, the π bonding is more important than the σ bonding, though the pKa of CN^- (9.04) is less than glycine (9.74), CN^- forms more stronger complex than glycine or glycine ester. In addition to the π bonding the binding of CN^- or imidazoles or histamine to Co(III) of cobaloximes can be attributed to soft-soft interaction, whereas binding of glycine or glycine ester to Co(III) can be attributed to soft-hard interaction. Soft-soft interaction gives more stability than soft-borderline or soft-hard interactions.

In an effort to understand the mechanism of B_{12} activation (Co-C bond cleavage) a number of model compounds have been used to study the 'trans effect', the effect of axial ligation on the Co-C bond. Since trans ligand plays important role in the Co-C homolytic cleavage we have studied the binding of various N donor ligands to cobaloximes to understand the nature of bonding, ability to bind and mechanism of binding. This will help in understanding the Co-C homolytic cleavage.

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Spectrophotometric determination of stability constants of copper(II) complex with sulphur reagent (TQA) – Trend, structure and regression analysis

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Abstract

Three different chelate species related to bio-organic, essential and disease prone metal ion have been investigated by spectrophotometry. The forms of the chelate species include cationic, neutral and anionic in nature. The stepwise and overall stability constants were evaluated utilizing a new and novel method and compared utilizing H-M's equation. The standard methods have been followed to find the correlation, absorptivity and reproducibility based on regression analysis. The increased effect in trend i.e. $k_1 < k_2 < k_3$ are explained by π-electron systems and structural aspects. Their values obtained using three different methods agreed well with each other. The S.D., regression analysis for the copper (II)- TQA complex obtained by standard methods are excellent.

(**Keywords :** spectrophotometry/stability constants/copper/TQA/ regression analysis)

Introduction

The chromogenic activity has been found to be the matter of great inherent interest due to high molecular potency to form colored chelate. At trace level, the capability to form a chelate molecule which would be neutral charged and highly stable is rare. The chromogenic group containing a thiopeptide linkage sometime overcome this barrier in chelation[1]. The sulphur reagents are inherently and invariably inert and unstable. Moreover, the higher oxidation state of metal ion causes detrimental effect towards reagent instability. The chelational activity is dependent on ironic state, strong polarity and high polarizability of atoms within ligated chromogenic chain present in reagent molecule[2,3]. The sulphur atom is known to polarize the bond and activity of a chelating group. This can well explain high sensitivity, selectivity and almost specificity at ultratrace level for determination of metal by spectrophotometry. The activity of a particular metal ion, pH effect can create the required potential and electrical field to induce ligational property and molecular phase[4,5]. All these are conducive and can synchronize to give effective spectral transition (EST) with energy selective to chelate species. In case of absence of such synchronization there is no chelational property at the molecular phase. In fact, those chromogenic group which are active for electronic transitions are strongly effective in chelation[6]. It has been observed that a fused heterocyclic ring N-atom attached to thiopeptide linkage strongly influences the selective and sometime highly specific chromogenic towards chelation[7-9]. The chelation is highly selective and sensitive but the chelate is not absorbed by the substrates or surface active agents. None of the species are active towards micelles forming agents. In this paper, the chelate stability of all the species are compared, discussed and reported. The precision and reproducibility are reported by standard statistical methods[10,11].

Materials and Method

Apparatus : A Hilger – Uvispek and PE spectrophotometer (Hitachi 200) with 1-cm glass cells was used for absorbance measurements. The solution pH values were measured at room temperature with an ELICO-LI-10 (India) pH-meter having all purpose glass electrode.

Reagents : An accurately weighed quantity of copper sulphate pentahydrate was dissolved in double distilled water and standardized by the α-benzoinoxime

method[12]. A 01.% (w/v) reagent solution in pure ethanol was used. A 0.1 M HCl was used to adjust the pH in the measurements. All other chemicals used were of G.R. grade. The reagent was synthesized by Willgerdot's reaction. It was isolated following Porter's method[13]. The yellow crystals have the m.p. 109±1°C.

Procedure : A definite aliquot of standard copper (0-100 μg/ml) solution was transferred with a pipette in a 25ml flask. A few drops of 0.1M HCl were added to it, followed by 5ml of 0.1% alcoholic reagent solution and 7.5 ml of pure ethanol. The volume was made up with water and the contents were mixed thoroughly (pH=2.7). A reagent blank prepared in identical way showed neligible absorbance. The absorbance of the blue-violet complex was measured at 550 nm against water blank. Prepare a calibration curve and measure the absorbance of the unknown solution with or without spiking of the analyte solution mixture.

Determination of the composition : A 1:3 metal to ligand ratio was determined by methods of continuous variation[14] and mole ratio[15]. An equal molar solution of metal and reagent were used following the recommended procedure. The absorbance were measured at 550 nm by the procedure. The equal molar concentrations, Cu(II) ≡ TQA ≡ 1.574×10^{-3} M were utilized and the volume was made up to 25 ml. The final concentration of the metal was 6.3×10^{-5} M. Both the methods have shown sharp break at the stoichiometric compositions. Three replicate solutions were prepared and used to confirm the Cu(II): TQA ratio to be 1:3. The result which gives highest accuracy and precision with minimum deviations using Harvey-Manning's equation is reported.

Results and Discussion

Chelate Characteristics : The chelating property of sulphur compound giving a thioureide group to induce selectivity have seen investigated. Copper(II) ion was found to be effective to produce spectral characteristics of the chelate even with ultra-trace amount. The spectra was found sufficient to investigate the composition, optimum limits of determination and tolerance limits or ratio interference effect, sensitivity, stability and major application with standard BAS samples. The chelate is highly stable in all most all the polar solvents, but accuracies and precision is better in acetone and fifty percent alcohol. The violet complex is non-extractable in other polar and non-polar solvents. The surfactants such as CTAB, SDS, Triton-X-100 are not found to be the good absorbent or substrate to enhance sensitivity and extract ability for recovery with separation. The band position is not shifted and remained stable and specific with the bio-active species irrespective of different dielectric media[16,17]. The term specificity is appropriate because the physico-chemical properties are not induced and influenced by environmental effects and change in experimental conditions.

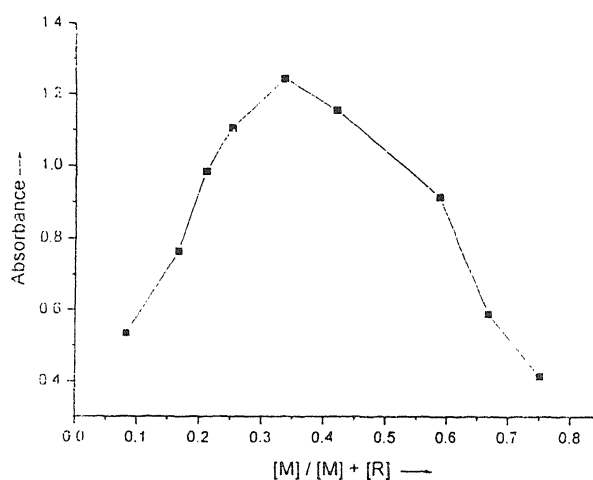



Fig. 1 – Job's Plot (method of continuous variation) $M = R = 1.5748 \times 10^{-3}$ M

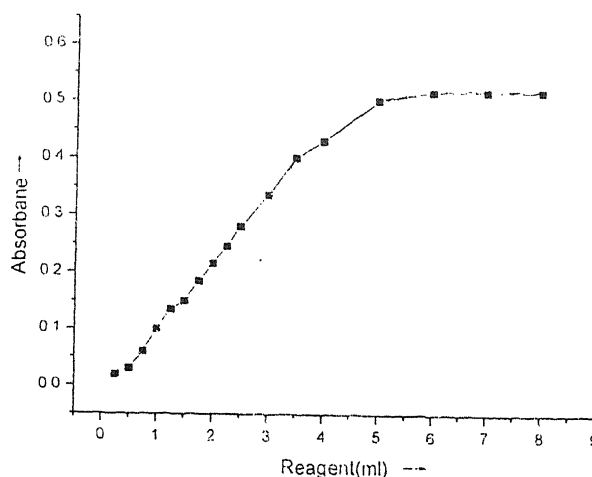



Fig. 2 – Mole-Ratio Plot. $M = R = 1.5748 \times 10^{-3}$ M Metal taken = 1 ml of 1.573×10^{-3} M.

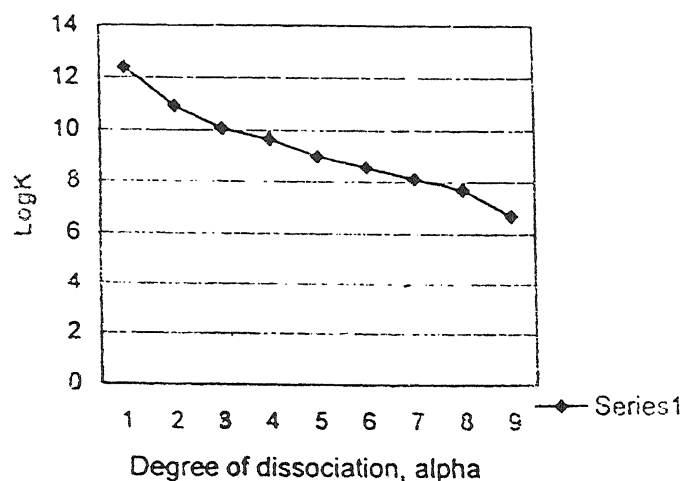



Fig. 3 – Plot of $\log^k$ *vs.* degree of dissociation, alpha.

Table 1 –Determination of stepwise and overall stability of 1:3 copper (II)-N-(Phenyl)-2-thioquinaldinamide (TQA) chelate in 50% ethanol at 25±1°C.
Photometric method based on Harvey-Manning's equation.

A_m	A_s	C,M	α	$\log^k{}_1$	$\log^k{}_2$	$\log^k{}_3$	$\log^k$
0.335	0.215	6.3×10^{-5}	0.3582	3.49	–	–	–
0.215	0.085	"	0.6046	–	4.42	–	–
0.515	0.335	"	0.3495	–	–	4.90	12.81

$\alpha = A_m - A_s/A_m$; $k_{1,2,3} = 1 - \alpha/\alpha^2.c$. Here $k_3 > k_2 > k_1$

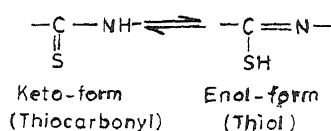
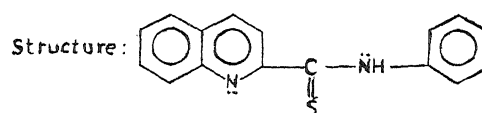
II. Methods of determination of stepwise and successive stability constants of copper (II) – TQA and statistical analysis.

Methods/ Equations	Stepwise stability constants $\log^k{}_{1,2,3}$	Overall stability constant $\log^k$	Average value $\log^k{}_{1,2,3}$ $\log^k$	S.D. or s
Harvey-Manning	$\log^{k_1}$ – 3.49 $\log^{k_2}$ – 4.42 $\log^{k_3}$ – 4.90	12.81	$\log^{k_1}$ – 3.47 ±0.03	±0.03
Yatsimirskii	$\log^{k_1}$ – 3.47 $\log^{k_2}$ – 3.95 $\log^{k_3}$ – 5.28	12.70	$\log^{k_2}$ – 4.19 ±0.24	±0.24
Leden	$\log^{k_1}$ – 3.44 $\log^{k_2}$ – 4.20 $\log^{k_3}$ – 5.06	12.70	$\log^{k_3}$ – 5.08 ±0.19	±0.09
			$\log^k{}_{ov}$ – 12.73 ±0.06	±0.06

±Represent standard deviation, S.D. %RSD = ±9.05, ±6.35, ±2.13, *t*, *r* (*N*=3,4) : *t* = 1.71, 1.98, 1.82, 2.1 and *r* = 0.8, 0.9, 0.8, 0.8 $\log^k{}_{ov}$ = 12.73±0.06.

Reagent : N-(Phenyl)-2-Thioquinaldinamide

Structure :

Keto-form (Thiocarbonyl) ⇌ Enol-form (Thiol)

Thio-peptide group : –C(=S)–NH–

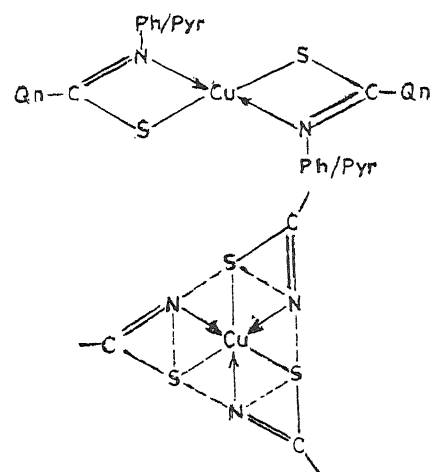
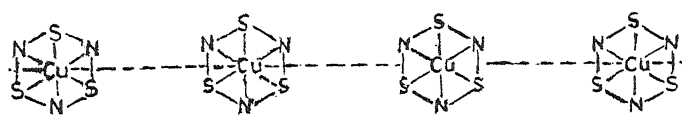
Azomethine group : >C=N–

1:3 Copper chelate

Polymeric chain

Fig. 4 – Schematic diagram for the composition structure, stability and three different species of the copper (II) – N-(phenyl)-2-thioquinaldinamate complex.

Table 2 – Determination of stability constants evaluated by different methods and comparison with extrapolation method and statistical analysis.

Sl. No.	Method based on eqns.	$\log^{k_1}(\beta)_1$ $\log^{\beta_1}$	$\log^{k_2}(\beta_2/\beta_2)$ $\log^{\beta_2}$	$\log^{k_3}(\beta_3/\beta_2)$	$\log^{k}/\log^{\beta_3}$ S.D.
1.	Leden's	3.44	4.20	5.06	12.70±0.32
		3.44	7.64		12.70±0.32
2.	Harvey-Manning's	3.49	4.42	4.90	12.81±0.32
3.	Method of extrapolation of $\log^k$ *vs.* α	$\log^k_{\text{exrap.}}$			13.30

± Represent standard deviation, S.D. %RSD = ±11.6. *t*, *r* (N=3) t=1.3 and r=0.8.

Thermodyanamic stability constants : The stepwise and overall stability constants[18] were determined by applying Harvey-Manning's equation. The reagent, TQA, formed a 1:3 (M:R) complex at pH 2.7 and absorbance are measured at 550 nm and these are depicted in Fig (1-3). The degree of dissociation, $\alpha = (A_m - A_s)/A_m = 0.215 - 0.085/0.215$ (1:1 species), $\alpha = 0.335\text{-}0.215/0.335$ (1:2 species) and $\alpha = 0.515\text{-}0.335/0.315$ (1:3 species) for 1:1,1:2 and 1:3 copper- TQA chelate and mole-ratio data were utilized to obtained $\log^{k_1}$, $\log^{k_2}$, $\log^{k_3}$ and $\log^k$. Their values were found to be 3.49, 4.42, 4.90 and 12.81. respectively at 25±1°C in 50 percent ethanol-water solvent. The $\log^{k_1}$ was also obtained by difference using $\log^k$ to be 12.81. The $\log^{k_1}$ value can also be determined considering minimum absorbance (A_s) at stoichiometric composition just near at the beginning of formation of 1:1 species. The reagent absorbance should be equal to or less than 0.005 ± 0.004 within 96% percent confidence limit. The results are given in Table 1. The present method has several advantages due to its simplicity, rapidity with quantitative equilibrium states, high level of precision and reproducibility. Also, the method provided excellent results of regression analysis when compared with other methods.

In the extrapolation method, the different $\log^k$ values obtained from corresponding α values in the mole-ratio curve were plotted against α when a linear plot having a negative slope was obtained. $\log^k$ values sharply increase with free-ligand, [L]. $\log^k_{\text{extrapol}}$ was obtained to be 13.30 by this extrapolation method as shown in Fig 3. It agreed well with variation within 0.5 in log unit or a deviation of 3.8% in overall values of acceptable limit in absence of sufficient amounts of reagent. The result have shown excellent agreeable limit with those obtained by Leden's and Harvey-Manning's equation. A difference in $\log^k$ values of more than 1 unit once again proved that polymeric unit of copper (II) thiolate is slightly dissociating in nature. Moreover, formation steps are combined with overlapping criteria and influence of tautomeric nature of keto-enol forms in absence of sufficient reagent.

After complete formation of 1:1 CuL_1 species, 1:2 CuL_2 species begins to form and afterwards 1:3 $HCuL_3$ is formed in solution. The complexes are formed in a stepwise fashion, but still there exist a competetive force to complex in otherwise in successive manner. Both the equilibrium system will operate simultaneously and they will combine and merge together by permutaion and combination in solution phase. This will create an cverlapping phenomenon in a monomer. In the solid state formation, this will lead to a tendency to polymerize giving a tetramer.

Stability sequence and statistical regression analysis : With thioureide group the trend on stepwise constants are found to be reversed i.e. $k_3 > k_2 > k_1$ in all such methods of evaluation. But, the K_{ov} value is nearly the same. There are variations in the respective stepwise values (k_1, k_2, k_3) but the difference is very close to the observed intel structures for separate chelate units. The statistical regression analysis on k_1, k_2, k_3 and K values has been made by standard methods to obtain the range of accuracy and reproducibility. Those were followed to calculate S.D., %RSD and r, as correlation coefficient[11,19]. All the essential parameters to check those values were calculated and described in the text. The results summarized in Tables (2&3) have shown excellent reproducibility within 99±0.5 percent of confidence limits. The standards deviations (s or S.D.) and correlation coefficient (r) values lie well within the acceptable limit of precession for $k_{1,2,3}$, K and the values are ±0.03, ±0.27, ±0.19, ±0.06 and 0.86, 0.89, 0.88, 0.90, (N=3) respectively.

Formation and stability of chelate species : The keto-enol form of thiopeptide group acts both as a

bio-active group and a highly active chromogenic[20,21] group. The wide range of detection and stability of chelate formation is very much sensitive to π-ring linked either to N-or S-atom of the thio-peptide chain, temperature, pH, homogeneities and distribution of chelate species to solvent phase. The solvent effective responsive stability (SERS) of different metal species protects the molecular existence of the complex. The spectral signals of chelate species remained undisturbed by environmental interactions for a short-term or limited period. In most cases, it is the thermal or temperature effect which destroys the signal stability of spectral band of a complex in solvent. The reagent itself acts as a morphine by way of heat conduction due to flow of micro-current within the chelate ring. The chelate complex is found to be stable for several months in refrigerator, but to is stable only for six hours at room temperature. The thioquinaldinamide with presence or absence of ring nitrogen with greater possibility of electron delocalization showed high chromogenic property towards chelation and stability both at acid and alkaline pH ranges. The moral absorptivities of 1:1 and 1:2 copper (II) species are almost identical and these are five times less intense than ultimate final 1:3 (ML_3) species. The 1:1 square planar molecule $[Cu(H_2O)_2L]Cl$ is cationic in nature and it is less stable compared to neutral square planar 1:2 structure CuL_2 of higher stability. It can be extracted in non-polar medium. The 1:3 copper chelate anionic in nature offers maximum highest stability with minimum interactions, increased number of π-rings, stereochemically stable octahedral structure and polymerization[21].

Influence of solvent dielectric and micro-current : The solvent dielectric greatly influences the process of dissolution of charged and neutral chelate species with interfacial transfer from one phase to the other and *vice-versa*. The volume of the diluent has been found to be the prime factor for solubility and stability in solvent mixture. Presence of other ions superceed the dielectric effect and the tolerance limits are widely affected. The micro-current generated in the chelate ring nucleus are drifted from the metal complex and the tolerance limits have been observed with interfering ions. Depending upon the extent of such effect the stepwise formation constant ($k_{1,2,3,}$ K) did not differ at all in ultra-trace speciations and the difference in values are very much negligibie in comparison. Presence of π-rings and effect of micro-current indicated strong influence on the tolerance limits. The increased number of π-rings have increased the chances of in and out flow of micro-current giving large variation of tolerance limits. In the process the chelation starts with delayed time effect because of greater extent of interaction with the ligand environ-ment. When the number of π-rings are evenly poised on both sides of a chelating group, a natural balance of flow of π-currents results. Strong chelation and simultaneous bond formation, increased π-bonds with greater stabilizing effect minimizes the overlapping criteria. Depending on such extent the K values become close to each other. Moreover, the balanced flow of π-current, the reagent and the method become more specific in nature. The tolerance limits have increased to a maximum limit. The term reagent specificity is thus appropriate for ultra-trace determination of the bio-inorganic copper (II) ion using TQA as chromogen. Thus, the involvement of π-rings and effect of micro-current on the tolerance limits in ultra-trace determination have been explained. The increasing effect of π-current in chelate ring nucleus resulted a more stable state of configuration. Thus, it can well explain the increasing trend of higher order during stronger chelation.

The structural aspects : The tautomeric forms of the reagent, reported octahedral structure and structures of different chelate species are given in the schematic representation and shown in Fig 4. The nature of the ligand or its denticity are shown in the structures indicating mode of coordination. Only the thio-peptide group is coordinated to generate its tendency to polymerize giving outstanding thermal stability with high m.p. The reagent is normally bidentate with quinoline ring N-atom and –SH group bonded to H in reagent itself and copper in different solvents. The denticity is much susceptible and changes with induced dielectric properties of the varying nature of solvents. More likely, the thio-peptide group is an active chromogen to influence on the other hand high chelational property even forming 4-membered ring chelate with thio-peptide chromophoric group. In this way it expands its structural chain and stereo-chemical configuration till a highly stable polymeric unit comprising a stable tetramer is formed in the solid state. The nature of the 1:3 Cu- TQA complex is anionic in solvent as

the monomer phase. The square planer dichloro – species is also formed, but it is very unstable and immediately converts to square phyramidal aquo complex. The 1:2 CuL_2 is a neutral complex with increased stability value due to complete chelation. Under the strong ligand field effect and the tendency of copper (II) to form octahedral complex, $HCuL_3$, pairing still higher stability to the anionic species. The three different species are formed with their individual stability factors and overlapping criteria only at equilibrium. The spectra of 1:3 chelate corresponds to that of $HCuL_3$ molecule under the influence of dielectric constant. This leads to formation and existence of three different species i.e. cationic, neutral and anionic nature at equilibrium. This explained the occurrence of nature and hence, the stability sequence. In the solid state the complex is polymeric due to ligand structure and contains a tetramer having a cyclic ring unit embedded together to form a benzene-like structure with polymeric chain. From IR spectra in nujol mull, the nature of coordinating groups is confirmed through stretching modes and their frequencies of absorptions by chromophoric linkage in the reagent and complex.

Conclusion

The reagent TQA, formed with copper(II) a blue-violet 1:3 (Cu : TQA) anionic complex at pH 2.7 in 1:1 ethanol – water mixture. The composition was confirmed by methods of continuous variation and mole-ratio. Elemental analysis. UV-visible and IR spectra of reagent and complex $H[Cu(TQA)_3]$ firmly established the M:R ratio. The thermodynamics equilibrium constants have been determined by a new and novel method utilizing H-M's equation and agreed well. The Newton-Raphson's method with computer programming was followed and $\log^k$ found to be 12.81 at 25±1°C. Almost identical $\log^{k}{}_{1,2,3}$ and $\log^k$ values were found. The trend of the stepwise constants was found to be in increasing order, $k_1 < k_2 < k_3$. The sulphur reagent showed varied nature of the bio-active chromogenic group. The mechanism of formation is supported by specificity of the thiopeptide group over a wide pH range 1.5 and 3.7 for the bio-inorganic copper (II) ion. The ionic chelate is much stable due to alternate arrangement of N, S-atoms forming a hexagonal thermally stable cage with copper ion at the center of highly stable inorganic benzene like structure. The precision level and accuracies have been determined by standard methods and statistical regression analysis. The standard deviations (S.D. or s) on equilibrium constants are ±0.03, $\log^{k}{}_1$; 0.27, $\log^{k}{}_2$; ±0.19, $\log^{k}{}_3$; and ±0.06 and $\log^k$. The % RSD values are ±1.01, $\log^{k}{}_1$; ±9.05, $\log^{k}{}_2$; ±6.35, $\log^{k}{}_3$; ±2.13, $\log^k$ for the stepwise and overall stability constants of ML_3 species. The correlation coefficient, r, is > 0.9 for each of $\log^{k}{}_1$, $\log^{k}{}_2$, $\log^{k}{}_3$, and $\log^k$, n=3 and they have shown excellent precision and reproducibility. The ultra-trace determination and analysis have also shown high precision.

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Synthesis of hydrocarbons alongwith other possible products through decarboxylation of potassium salt of palmitic, lauric and myristic acid in aqueous solution at platinum-anode

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Abstract

The electrochemical oxidation (i.e., anodic decarboxylation) of potassium-salt of palmitic acid, lauric acid and myristic acid was carried out in aqueous solution for the purpose of investigating this type of oxidation as a possible synthetic procedure for the preparation of saturated hydrocarbons (dimer), esters (straight and branched chain) and alkenes etc. The products formed during electrolysis at constant-anode potential have been analysed by mass and I.R. spectra, and are reported here.

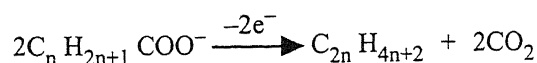
(Keywords : electrochemical oxidation/anodic decarboxylation/ Green chemistry/ constant potential electrolysis/electro organic synthesis)

Introduction

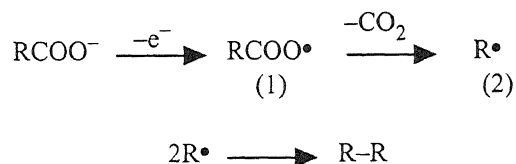
Electrode processes in the realm of organic reactions are accredited[1] over conventional organic processes with some specialities such as anode and cathode, whose potentials can be controlled at will, acts as oxidant and reductant for a substrate. Electro-organic reactions can be carried out at room temperature and these are essentially non-polluting and as such are part of Green chemistry.

In the present paper the result of our studies on anodic-decarboxylation of three higher fatty acids *viz.* palmitic acid, lauric acid and myristic acid with subsequent formation of dimer and several other expected products at definite anode-potentials are reported.

The reaction that forms the dimer of the alkyl radical will be referred to here as the Kolbe reaction. It is outlined as follows :

$$2C_n H_{2n+1} COO^- \xrightarrow{-2e^-} C_{2n} H_{4n+2} + 2CO_2$$

Good reviews of the Kolbe reaction are available[2-4]. Weedon has discussed the optimal experimental procedures for the Kolbe reaction[2]. Best yields (50-95%) of dimer are obtained when the carboxylic acid is partially neutralized, followed by oxidation at low voltage at a platinum anode in methanol[2] or dimethylformamide[5]. Under these conditions, the carboxylate anion undergoes1-electron oxidation to an aceloxy radical (1) which looses CO_2 to form radical (2), which dimerises. However, there are some special features involved in this dimerisation.

$$\underset{}{RCOO^-} \xrightarrow{-e^-} \underset{(1)}{RCOO\bullet} \xrightarrow{-CO_2} \underset{(2)}{R\bullet}$$

$$2R\bullet \longrightarrow R\text{–}R$$

Vijh and Conway[3] have summarized the evidence that the Kolbe oxidation involves a film of adsorbed intermediates. They have reported that the ratio of coupling to disproportionation products in the Kolbe reaction is much higher than when the same radicals are generated in homogeneous solution. Another surprising feature of the Kolbe reaction is that it occurs at more positive anode potential than the oxidation of solvent itself. Apparently the adsorbed film inhibits oxidation of the solvent and permits a potential to be attained where oxidation of the carboxylate ion can occur[6].This allows the preparative scale electrolysis to be carried out with simple experimental apparatus. Since this adsorption process governs the anode potential, it is not necessary to use a potentiostat to control the potential.The electrolysis can be carried out at constant current instead of constant potential.

Materials and Method

For the purpose of synthesis of straight-chain saturated hydrocarbons alongwith significant possible products, we took 50 C.C of 0.1N aqueous solution of potassium-salt of fatty acids (potassium-salt of fatty acid is prepared by continually adding drop-by-drop aqueous solution of KOH and phenolphthalein indicator is used to assess the complete neutralization) in a reaction bottle alongwith 50 C.C of 1.0N aqueous KNO_3 used as supporting electrolyte

Singh *et al.*[7] have carried out a number of reactions with Pt electrode. For constant-potential electrolysis, three-electrode cell assembly with platinum (flattened sheet of dimension 1cm x 0.5cm) as working as well as counter electrodes and saturated calomel electrode (SCE) as reference-electrode was used. The platinum-electrodes are surrounded from one side with glass-material and SCE connected with electrolyte through a long bent tube in which Agar-Agar with KCl is filled.

Palmitic acid, lauric acid, myristic acid, mercury, KNO_3, KCl, KOH were of AnalaR grade. Double-distilled water was used for preparation of solutions.

In each case the electrolysis was carried out at controlled anode-potentials for one hour. Sharma *et al.*[8] have also discussed some reactions at constant potential. The current-potential data was recorded at an interval of 10 min. and are reported in Table 1. As a result of electrolysis the solid products having density less than the bulk, were filtered by sintered-glass G_4-crucible. The filtered solid products were then dried below their m.p. in hot air-oven and analysed by mass and I.R. spectra.

Table 1 – Current – potential data of electrolysis as recorded by potential-cum-galvanostat

Potassium salt of palmitic acid

Time interval	Potential (mV)	Current (mA)
0.00-0.10h	1900	0.45
0.10-0.20h	1800	0.22
0.20-0.30h	2000	0.30
0.30-0.40h	1840	0.29
0.40-0.50h	1850	0.30
0.50-1.00h	1800	0.29

Potassium salt of Lauric acid

Time interval	Potential (mV)	Current (mA)
0.00-0.10h	1000	0.31
0.10-0.20h	1040	0.28
0.20-0.30h	1090	0.35
0.30-0.40h	1090	0.38
0.40-0.50h	1050	0.38
0.50-1.00h	1090	0.38

Potassium salt of Myristic acid

Time interval	Potential (mV)	Current (mA)
0.00-0.01h	1390	0.78
0.10-0.20h	1400	1.18
0.20-0.30h	1400	1.15
0.30-0.40h	1410	1.15
0.40-0.50h	1400	1.18
0.50-1.00h	1400	1.16

Result and Discussions

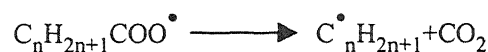
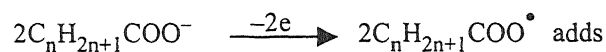
Anodic oxidation of aliphatic carboxylate ion causes decarboxylation and yields a variety of products: saturated and unsaturated hydrocarbons, esters, alcohols and ethers.

Reaction mechanism and possible products :

Several mechanisms have been advanced to account for Kolbe dimer formation. The ion-discharge theory of Brown and Walker[9] is shown as follows:

$$2C_nH_{2n+1}COO^- \xrightarrow{-2e} 2C_nH_{2n+1}COO^\bullet \text{ adds}$$

$$C_nH_{2n+1}COO^\bullet \longrightarrow C^\bullet{}_nH_{2n+1} + CO_2$$

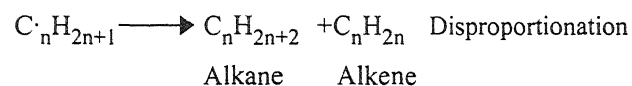
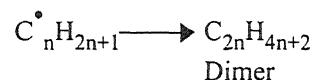
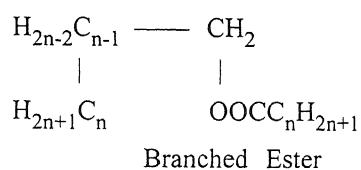
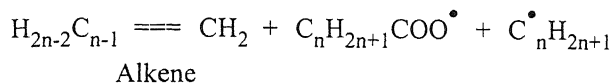
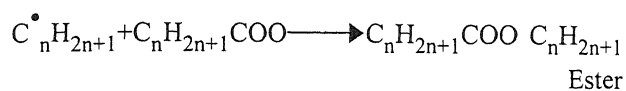
$$2C^\bullet{}_nH_{2n+1} \longrightarrow C_{2n}H_{4n+2} \quad \text{Dimer}$$

Several possible products due to free–radical[10] are as follows :

$$C^\bullet{}_nH_{2n+1} \longrightarrow \underset{\text{Dimer}}{C_{2n}H_{4n+2}}$$

$$C^\cdot{}_nH_{2n+1} \longrightarrow \underset{\text{Alkane}}{C_nH_{2n+2}} + \underset{\text{Alkene}}{C_nH_{2n}} \quad \text{Disproportionation}$$

$C^{\bullet}_nH_{2n+1} + C_nH_{2n+1}COO \longrightarrow C_nH_{2n+1}COO\ C_nH_{2n+1}$
Ester

$H_{2n-2}C_{n-1} === CH_2 + C_nH_{2n+1}COO^{\bullet} + C^{\bullet}_nH_{2n+1}$
Alkene

$$\begin{array}{ccc} H_{2n-2}C_{n-1} & — & CH_2 \\ | & & | \\ H_{2n+1}C_n & & OOCC_nH_{2n+1} \end{array}$$

Branched Ester

This branched ester is high molecular weight compound as shown in mass-spectra of the products.

Analysis of the product (s)

(i) The products are fairly insoluble in most of the known common solvents. This shows that non-polar character is predominant in the products.

(ii) The mass-spectra of the products shows various *m/e* peaks.

The *m/e* values for various products obtained by the electrolysis are given as follows.

Product	Formula

1. In case of potassium salt of palmitic acid ($C_{15}H_{31}COOK$)

(i) Dimer $C_{30}\ H_{62}$ (1) *m/e* = 422.8

(ii) Disproportionated Products (a) Alkene $C_{15}H_{30}$ (2) *m/e*=210

(b) Alkane $C_{15}H_{32}$ (3) *m/e*=212

(iii) Ester

(a) straight chain $C_{15}H_{31}OOCC_{15}H_{31}$ (4) *m/e*=466

(b) Branched chain $\begin{array}{ccc} H_{28}C_{14} & — & CH_2 \\ | & & | \\ H_{31}C_{15} & & OOCC_{15}H_{31} \end{array}$ (5) m/e=677

2. In case of potassium salt of lauric acid ($C_{11}H_{23}COOK$)

(i) Dimer $C_{22}\ H_{46}$ (6) *m/e* = 310

(ii) Disproportionated product (a) Alkene $C_{11}H_{22}$ (7) *m/e*=154

(b) Alkane $C_{11}H_{24}$ (8) *m/e*=156

(iii) Ester

(a) straight chain $C_{11}H_{23}OOCC_{11}H_{23}$ (9) *m/e*=354

(b) Branched chain $\begin{array}{ccc} H_{20}C_{10} & — & CH_2 \\ | & & | \\ H_{23}C_{11} & & OOCC_{11}H_{23} \end{array}$ (10) *m/e*=508

3. In case of potassium salt of myristic acid ($C_{13}H_{27}COOK$)

(i) Dimer $C_{26}\ H_{54}$ (11) *m/e* = 366

(ii) Disproportionated products (a) Alkene $C_{13}H_{26}$ (12) *m/e*=182

(b) Alkane $C_{13}H_{28}$ (13) *m/e*=184

(iii) Acyl sp. $C_{13}H_{27}COO$ (14) *m/e*=228 (appox.)

The product No (5) and (10) are obtained as new products in Kolbe reaction performed by us. The *m/e* value is 677, and the characteristic (-C=O) stretching band due to ester present in the compound is also seen at 1735 cm^{-1}. This is the unique feature of our studies. The *m/e* values for product No. (5) and (10) are 677 and 508 respectively, which confirms the formation of above mentioned new products

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Thermal decomposition kinetics of Co (II) chelates of substituted chalcones

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Abstract

The thermal decomposition of Co(II) complexes of 3-(phenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one(HPHPO),3-(4-chlorophenyl)-1-(2'-hydroxynaphthyl) -- 2-propen-1-one (HCPHPO), 3 - (4 – methoxyphenyl) – 1 - (2'-hydroxy-napthyl)-2-propen-1-one (HMPHPO), 3-(3, 4-dimethoxyphenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (HDMPHPO) was studied by thermogravimetry. Mathematical analysis of the data has allowed us to determine various parameters using Freeman-Carroll equation, the integral method using the Coats-Redfern equation and the approximation method using the Horowitz-Metzger equation. The trend of the kinetic parameters was found to be different from that of the thermal stability order. The low values of *Z* suggest the slow nature of the reaction.

(**Keywords** : thermogravimetry/chalcones/cobalt complexes/ activation energy/frequency factor/activation entropy/ free energy of reaction/specific reaction rate constant.)

Introduction

Structural studies on several metal chelates of β-diketones and 2-hydroxycarbonyl compounds have been reviewed by Holm and O'Connor[1]. Very few systems have been reported[2] showing the relationship between thermal stability of metal chelates and structure of the chelating agents.Wendlandt and co-workers[3-6] and Hill and co-workers[7,8] studied the thermal properties of metal chelates with different types of complexing ligands. The metal chelates of divalent transition metals with some o-hydroxy-chalcones standout as a distinct class of o-hydroxy-carbonyl compounds with low spin square-planar configuration, which do not easily form adduct. Extensive conjugation was found to be responsible for the strong field nature of the ligand[9]. Chalcones usually exhibit germicidal[10] bactericidal[11], fungicidal[12], antiviral[13] and carcinogenic activities[14].

In continuation of our earlier work[15-22] on thermal decomposition kinetics of metal chelates, the present investigation deals with the thermal stability of the cobalt chelates of 3 - (phenyl) -1 - (2'-hydroxynaphthyl) – 2 – propen -1 –one (HPHPO), 3 – (4 – chlorophenyl) – 1 – (2'– hydroxynaphthyl) – 2 – propen – 1 –one (HCPHPO), 3 - (4 – methoxyphenyl) – 1 – (2'- hydroxynapthyl) – 2-propen – 1 – one (HMPHPO), 3 – (3, 4 – dimethoxyphenyl) – 1 – (2'-hydroxynaphthyl)-2-propen-1-one(HDMPHPO) and evaluation of kinetic parameters employing the differential Freeman-Carroll equation[23] the integral method using the Coats-Redfern equation[24] and the approximation method using the Horowitz-Metzger equation[25].

Materials and Method

The chalcones were prepared by the condensation of 2-hydroxy-1-acetonaphthone with benzaldehyde, chlorobenzaldehyde, methoxybenzaldehyde and dimethoxybenzaldehyde employing the Claisen-Schmidt condensation reported earlier[26]. The cobalt complexes of chalcones were prepared according to the procedure described in an earlier paper[27]. The purity of the sample was checked by elemental analysis. The thermograms were recorded using a Perkin-Elmer TGS-2 thermo balance in ambient air and at a heating rate of 6K min^{-1}.

Typical TG curves are presented in Fig. 1. Kinetic data are evaluated from these TG traces using the equations Table 1 (see Fig.2-4)

Results and Discussion

All the complexes are coloured powders which are insoluble in water. The elemental analysis of the

Table 1 - Kinetic data.

Chelate	Parameters	From Freeman-Carroll equation	From Coats-Redfern equation	From Horowitz-Metzger equation
$Co(HPHPO)_2.H_2O$	E^* (kcal mol^{-1})	3.29	2.98	9.89
	$Z(s^{-1})$	6.04×10^{-2}	2.81×10^{-3}	6.94
	ΔS^* (e.u.)	– 26.79	– 28.19	– 21.92
	G^*(kcal mol^{-1})	17.38	17.81	21.42
	K_r (Su^{-1})	5.72×10^{-2}	2.54×10^{-3}	6.18
$Co(HCPHPO)_2.H_2O$	E^* (kcal mol^{-1})	4.92	3.09	12.27
	Z (s^{-1})	2.94×10^{-1}	8.46×10^{-3}	96.28
	ΔS^* (e.u.)	– 25.64	– 31.81	– 22.89
	G^* (kcal mol^{-1})	18.97	20.52	24.81
	K_r (Su^{-1})	2.85×10^{-1}	8.27×10^{-3}	95.58
$Co(HMPHPO)_2.H_2O$	E^* (kcal mol^{-1})	8.45	12.05	15.09
	Z (s^{-1})	1.37	3.08×10	4.06×10^2
	ΔS^* (e.u.)	– 24.78	– 21.42	– 19.14
	G^* (kcal mol^{-1})	22.20	23.94	25.71
	K_r (Su^{-1})	1.29	30.40	4.01×10^2
$Co(HDMPHPO)_2.H_2O$	E^* (kcal mol^{-1})	9.75	15.04	17.18
	Z (s^{-1})	3.96	4.69×10^2	$44 .54 \times 10^2$
	ΔS^* (e.u.)	– 23.79	– 21.26	– 19.08
	G^* (kcal mol^{-1})	22.52	25.86	26.71
	K_r (su^{-1})	3.37	4.14×10^2	44.72×10^2

Table 2 - Thermal decomposition data.

Chelate	Decom-position-temp. (^0C)	Residue (Percentage) Theoretical		Experi-mental	Free-man Carroll method
		Metal	Oxide	Metal Oxide	
$Co(HPHPO)_2.H_2O$	240	9.75	13.27	13.27	1.09
$Co(HCPHPO)_2.H_2O$	232	8.75	11.91	12.47	1.16
$Co(HMPHPO)_2.H_2O$	254	8.87	12.07	11.89	1.18
$Co(HDMPHPO)_2.H_2O$	271	8.14	11.07	11.92	1.06

chelates showed cobalt to ligand ratios of 1:2. Further the TG curves revealed that cobalt complexes are monohydrated[28-30]. The complexes were found to be stable in air and non-hygroscopic. The residue obtained from thermogravimetric runs of each of the chelates was weighed to determine whether or not it might be a meatal oxide. The theoretical and observed percent weights remaining for the metal chelates assuming the residues to be metal oxides .The final pyrolysis product of all the complexes corresponds to Co_3O_4. The thermal stability data (Table 2) of the chelates reveal that the introduction of a – OCH_3 group increases the thermal stability, where introduction of a chlorine atom decreases the the thermal stability. The enhancement in thermal
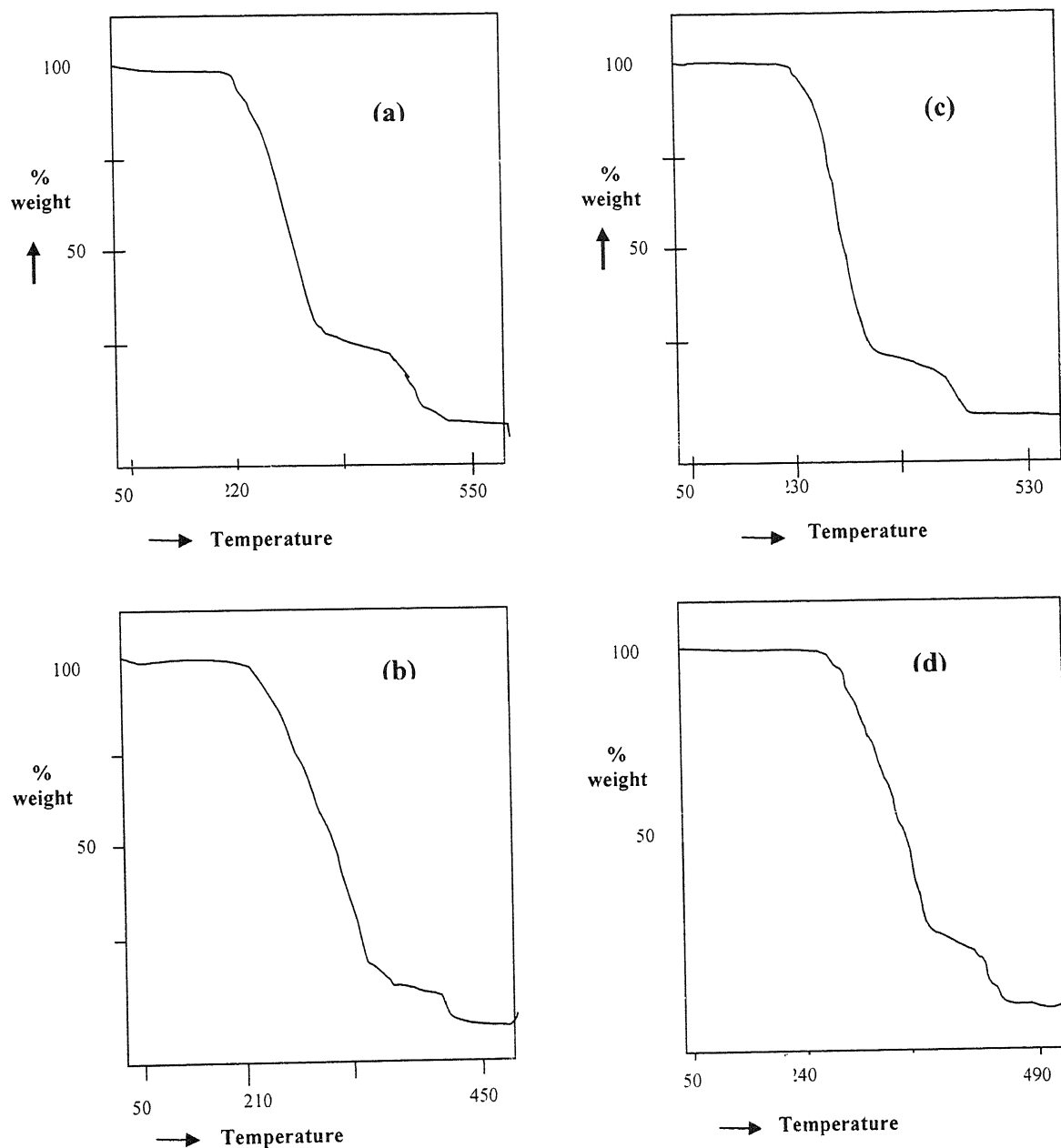
Fig. 1 – Thermograms of (a) $Co(HPHPO)_2.H_2O$, (b) $Co(HCPHPO)_2.H_2O$, (c) $Co(HMPHPO)_2.H_2O$, and (d) $Co(HDMPHPO)_2.H_2O$.

stability by the presence of electron releasing – OCH_3 groups at position 3 and 4 was ascribed to the availability of higher electron density at the reactive centre. The lower thermal stability of CPHPO may be attributed to the electron withdrawing effect of a chlorine atom, leading to lower electron density at the reactive centre. The relative thermal stability of the chelates is $Co(HCPHPO)_2.H_2O$ < $Co(HPHPO)_2.H_2O$ < $Co(HMPHPO)_2.H_2O$ < $Co(HDMPHPO)_2.H_2O$. Mathematical analysis of the TG curves was carried out using the differential Freeman-Carroll equation, the integrat method using the Coats-Redfern equation and the approximation method using the Horowitz-Metzger equation.

Freeman-Carroll equation

Freeman-Carroll equation which may be written in the form
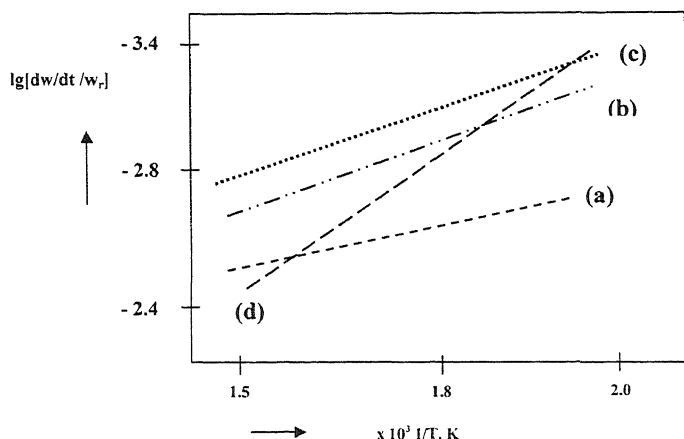
Fig. 2 – Freeman-Carroll plots of (a) $Co(HPHPO)_2.H_2O$; (b) $Co(HCPHPO)_2.H_2O$; (c) $Co(HMPHPO)_2.H_2O$, and (d) $Co(HDMPHPO)_2.H_2O$

Fig. 3 – Coats-Redfern plots of (a) $Co(HPHPO)_2.H_2O$; (b) $Co(HCPHPO)_2.H_2O$; (c) $Co(HMPHPO)_2.H_2O$, and (d) $Co(HDMPHPO)_2.H_2O$

$$\frac{\Delta \log(dW/dt)}{\Delta \log W_r} = \frac{-\left(E^*/2.303R\right)\Delta\left(T^{-1}\right)}{\Delta \log W_r} + n$$

where $W_r = W_\alpha - W$, W_α is the mass loss at the completion of reaction, W is the mass loss up to time t, T is the absolute temperature at time t, n is the order of reaction. R is the gas constant in calories and E^* is the energy of activation in K cal mol^{-1}. W_r and T can be directly obtained from the TG traces. The temperature slopes dW/dT were converted into time slopes dW/dt, using the relation[31]

Fig. 4 – Horowitz-Metzer plots of (a) $Co(HPHPO)_2.H_2O$; (b) $Co(HCPHPO)_2.H_2O$; (c) $Co(HMPHPO)_2.H_2O$, and (d) $Co(HDMPHPO)_2.H_2O$

We obtain

$$\log\left(\frac{dW/dt}{W_r}\right) = \frac{E^*}{2.303RT} + \log Z$$

Plot of log $[(dw/dt)/W_r]$ against T^{-1} were drawn. They gave straight lines in all cases with slopes $-E^*/2.303R$ from which E^*values were obtained. Z was calculated from the above equation and the entropy of activation ΔS^* ,free energy of activation G^* and specific reaction rate K_r was calculated [32,33].

Coats-Redfern equation

$$\log\left[\frac{\ln\dfrac{W_\infty}{W_\infty - W}}{T^2}\right] = \log\left[\frac{ZR}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT}$$

where W_∞ = mass loss at the completion of the reaction, W = mass loss at time, Z = frequency factor, Φ^* = linear rate of heating and E^* = activation energy of the reaction.

Assuming the decomposition of Co(II)-chalcone chelates to follow first order kinetics (n=1) a plot of $\log\{\ln[(W_\infty/(W_\infty - W)) / T^2]\}$ against $1/T$ was

drawn which gave straight lines in all cases with a slope of $-E^*/2.303R$ from which the activation energy was calculated.

Horowitz-Metzger equation

$$\log \log \frac{W_\infty}{W_r} = \frac{E^* \phi}{2.303RT_s^2} - \log 2.303$$

where, W_∞ = mass loss at the completion of the reaction, $W_r = W_\infty - W$, W = mass loss at time t, T_s = peak temperature, R = gas constant.

A plot of log log W_∞ / W_r against θ was drawn which gave straight lines in all the cases with the slope $E^*/2.303RT_s^2$ from which E^* values were obtained.

Decomposition kinetics

The analysis of data using the Freeman-Carroll equation gives the order of the decomposition reaction near unity for these complexes. The values of activation energy E^* obtained by all three methods for the cobalt chelates are given in Table 1. The negative values of ΔS^* indicates that the activated complex has a more ordered structure than the reactants[34] and that the reactions are slower than normal, further the low values of Z suggest that the decomposition reaction of the polychelates can be classified as a slow nature of the reaction[35,36].

The values of E^* and Z increase in the order $Co(HPHPO)_2.H_2O$ < $Co(HCPHPO)_2.H_2O$ < $Co(HMPHPO)_2.H_2O$ < $Co(HDMPHPO)_2.H_2O$.

The kinetic parameters show a somewhat different trend from that of thermal stability. This can be due to the fact the decisive criteria in kinetics are often quite different from those which decide thermal stability.

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Development and validation of neutralisation reaction based analytical methods for the assay of atenolol in pharmaceuticals

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Abstract

Visual titrimetric, pH-metric, conductometric and spectrophotometric techniques are described for the determination of atenolol in pure form and in pharmaceutical formulations. Visual titrimetric method is applicable over 2-20 mg range whereas pH-metric and conductometric methods can be applied over a range 10-60 mg of atenolol. In spectrophotometry, Beer's law is obeyed over the concentration range 3.0-30.0 $\mu g\ ml^{-1}$ with an apparent molar absorptivity of 3.47×10^3 $l\ mol^{-1}\ cm^{-1}$ and a Sandell sensitivity of 105 $ng\ cm^{-2}$. The limits of detection and quantification are calculated to be 4.61 and 15.38 $\mu g\ ml^{-1}$, respectively. Validation parameters for linearity, accuracy and precision are in agreement with the ICH guidelines

(**Keywords :** atenolol/visual titrimetry/pH metry/conductometry/ spectrophotometry/pharmaceuticals)

Introduction

Atenolol, 4-(2-hydroxy-3-isopropylamino propoxy) phenyl acetamide, is known as a beta-blocker in therapeutics and is widely used in the management of hypertension, angina pectoris, cardiac dysrhythmias and myocardial infarction[1]. The dosing and / or ageing of commercially available pharmaceutical preparations demand reliable methods for drug determination that are preferably selective, rapid and can be performed with simple equipment. This holds true for atenolol also.

A variety of techniques for the determination of atenolol in pharmaceuticals are found in the literature. Indian Pharmacopoeia[2],describes UV-spectrophotometric method for its assay in tablets where as British Pharmacopoeia[3] describes high-performance liquid chromatographic (HPLC) methods for its determination. The most widely used technique for the assay of atenolol has been HPLC and it has been used for the determination of the drug both in single[4-7] and combined dosage forms[8-12]. Other chromatographic techniques, such as liquid chromatography (LC)[13], thin layer chromatography (TLC)[14], HPTLC[15] and gas chromatography[16], have also been used to determine atenolol in pharmaceuticals. Methods based on self-fluorescence exhibited by atenolol in 0.1 M hydrochloric acid and phosphate borate buffer have been described for the sensitive determination of atenolol[17]. Atenolol in single[18] and combined dosage forms[19,20] has been assayed by UV-spectrophotometry. Although HPLC methods with UV and fluorescence detection are routinely used, these methods require complicated liquid-liquid or liquid-solid extraction steps and/or several complicated clean-up steps. They are time consuming and are often poorly reproducible.

There are only two reports[21,22] on the titrimetric determination of atenolol. The method of Gao and Wang[21] requires 200mg of drug for each trial for accurate results and the method reported recently by the present authors[22] has a narrow working range. The majority of the visible spectroohtometric methods [23-29] lack the sensitivity and simplicity required of routine analysis. The determination of atenolol based on the reaction with iron(III) chloride in acidic medium forming a reddish-violet ferric hydroxamate complex[26] has been reported, but the

sensitivity is too low (ε =570) and the procedure involves boiling for 20-30 min. The colorimetric method reported by Zakhari *et al.*[27], based on the reaction of drug with copper(I) and carbon disulphide involves multiple extraction steps besides being poorly sensitive (linear range, 8-56 $\mu g\ ml^{-1}$). The other colorimetric method[28] based on the reaction of atenolol with acetaldehyde and halogenated benzoquinones, also involves extraction step and use of an organic solvent as diluent. Recently reported[29] ion-pair extraction spectrophotometric methods using two dyes, Wool Fast Blue and Trapaeolin 000, are less sensitive (ε=623). The procedure reported by us recently[22] is based on the oxidation of atenolol by an excess of cerium(IV) followed by determination of residual oxidant *via* different approaches, although sansitive involves a number of experimental variables, in order to develop a simple, rapid, sensitive and accurate method for the routine analysis of atenolol, and a method that can be used in laboratories where modern expensive instruments such as spectrofluorimeter, HPLC or capillary zone electrophoresis cell are inaccessable. The methods described are based on the neutralization reaction involving the basic moiety of the drug molecule and hydrochloric acid.

Materials and Method

All absorbance measurements were made with a Systronics Model 106 digital spectrophotometer provided with matched 1 cm quartz cells. pH-metric titration was performed with an Elico Model LI-120 pH meter provided with a combined glass electrode-SCE system. Conductometric titration was carried out with an Equiptonics digital conductively meter Model No EQ-DCM-P for direct reading of specific conductance in the range 200 µmhos to 200 mmhos. A dip-type conductivity cell was used.

All chemicals used were of analytical grade and all solutions were made in distilled water except solutions for conductometric study which were prepared in triply distilled water.

Solutions of HCl, NaOH, bromothymol-blue-phenol red mixed indicator and phenol red (100 $\mu g\ ml^{-1}$) were prepared in the usual manner.

Pharmaceutical grade atenolol was procured from Cipla India Ltd., Mumbai, as gift and was used as received. A stock standard solution containing 2 $mg\ ml^{-1}$ atenolol was prepared by dissolving 500 mg of pure drug in water and diluting to the mark in a 250 ml calibrated flask. This solution (2 $mg\ ml^{-1}$) was used for titrimetric work, and for spectrophotometric work, the same was diluted appropriately with water to get a working concentration of 250 $\mu g\ ml^{-1}$.

Visual titrimetric method (VTM) : A 10 ml aliquot of drug solution containing 2-20 mg of atenolol was pipetted out into a 100 ml titration flask and 10 ml of 0.01 M hydrochloric acid was added into the flask by means of a pipette. After 20 min. the residual acid was back titrated with standard (0.01M) sodium hydroxide using two drops of mixed indicator. A blank titration was performed under identical conditions.

pH-metric method (PTM) : An aliquot (20ml) of standard drug solution containing 10-60 mg of atenolol was accurately measured into a 100 ml beaker. A glass – saturated calomel electrode was dipped in the solution. The solution was stirred magnetically and titrant (0.01, 02 or 0.05 M HCl) was added from a micro burette. Near the equivalence point, the titrant was added in 0.1 ml increments,. The titration was continued until there was no significant change in the pH on further addition of titrant.

Conductometric titration method (CTM) : A 30 ml aliquot of pure drug solution containing 10-60 mg of atenolol was accurately transferred into a 50 ml beaker and the initial specific conductance of the solution was recorded. Hydrochloric acid (5-10 times stronger than atenolol solution) was added from a micro burette in 0.25 ml equal increments. The mixture was stirred magnetically for 30 s after each addition and stable reading of specific conductance was recorded. The amount of drug was calculated from the amount of acid used in either method.

Spectrophotometric method (SPM) : One ml of 100 $\mu g\ ml^{-1}$ phenol red dye solution was accurately measured into a series of 10 ml calibrated flasks. Different aliquots (0.0, 0.25, 0.50 . . . . 1.50 ml) of standard 250 $\mu g\ ml^{-1}$ atenolol were added and the volume was diluted to the mark, mixed well

and absorbance of each solution measured at 430 nm against a water blank. The concentration of the unknown was read from the calibration graph or calculated from the regression equation..

Procedure for tablets : An amount of tablet powder equivalent to 500 mg of atenolol was weighed into a 250 ml calibrated flask, 60 ml of water was added and the mixture was shaken for 20 min; then the volume was made up to the mark with water, mixed well and filtered using a Whatman No. 42 filter paper. A suitable aliquot was then subjected to analysis by titrimetric methods. The tablets extract (2 mg ml^{-1}) was diluted suitably with water to get 250 μg ml^{-1} ATN and analysed spectrophotometrically by taking a convenient aliquot.

Results and Discussion

Method development : The proposed methods are based on the basic character of atenolol molecule and employ four techniques for the determination of the drug. Atenolol is weakly basic and direct visual titration was not feasible. Hence, the drug solution was reacted with a measured excess of hydrochloric acid, the residual acid being back titrated with sodium hydroxide. A contact time of 20 min. was found necessary for a quantitative reaction between atenolol and HCl. With 0.01M HCl and sodium hydroxide employed, bromothymol blue-phenol red mixed indicator gave a sharp end point and 2-20 mg of atenolol could be conveniently determined.

With pH-metric titration, a steep decrease in the pH was noticed at the equivalence point. In coductometric titration, the specific conductance was found to increase gradually in the beginning and increased sharply after the equivalence point, giving rise to ascending curves. The equivalence point was obtained by extrapolating the two straight-line poritions. With graphical endpoint location in pH-metric and conductometric titration methods, 10-60 mg of atenolol could be determined with reasonable accuracy and precision. The relation between drug amount and titration end point / equivalence point was examined, in all the three titrimetric methods. The linearity between the two parameters is apparent from the correlation coefficients of – 0.9986, 0.9892 and 0.9874 (n=5 in each case) obtained by the method of least squares for visual, pH-metric and conductometric titration methods, respectively. From this, it is implied that the reaction between atenolol and hydrochloric acid proceeds stoichiometrically in the ratio 1:1 in the ranges studied.

The spectrophotometric method using phenol red is based on the facts that the colour of the dye is controlled by the pH of the solution and that the colour change is not abrupt but occurs in a continuous manner over a definite range (transition range : 6.5-8) when the pH changes continuously. Phenol red changes its colour from yellow at lower pH to red at higher pH. When atenolol is added in increasing amounts to a fixed amount of phenol red dye (yellow colour), the pH is progressively increased, and as a result, the colour changes from yellow to red, and the yellow colour intensity decreases. This is indicated by the proportional decrease in the absorbance of the solution at 430 nm and is corroborated by the correlation coefficient, $r = -0.9856$.

In a preliminary study, 1 ml aqueous solution of 100 μg ml^{-1} phenol red in 10 ml was found to produce a convenient maximum absorbance at 430 nm. This absorbance decreased to a constant minimum when the dye solution was treated with 1.25 ml of 250 μg ml^{-1} atenolol solution in a total volume of 10 ml, thus limiting the upper Beer's law limit to 30 μg ml^{-1} . Beer's law is obeyed over 3 – 30 μg ml^{-1} atenolol in an inverse manner. The apparent molar absorptivity was calculated to be 3.47×10^3 l mol^{-1} cm^{-1} with a Sandell sensitivity of 105 ng ml^{-1}. The linear plot gave the regression equation :

$$A = 0.61 - 0.013\,C$$

where A is the absorbance at 430 nm and C is the concentration of drug in μg ml^{-1} with a correlation coefficient of - 0.9856 (n = 6). The limit of detection and limit of quantification were calculated to be 4.61 and 15.38 μg ml^{-1}, respectively. The measured dye colour was found to be stable for several hours in the presence of the drug.

Method validation

Accuracy and precision : The accuracy and precision of the methods were established by perfor-

ming seven replicate analyses on pure drug solution at three levels. The results of this study presented in Table 1 are indicative of good accuracy and precision. For a better picture of the reproducibility on a day to day basis, a series was run in which the standard solution at three levels was analysed for 5 days. In terms of standard deviation, the day to day coefficient of variation was less than 4% and represents the best appraisal of the precision of the procedures in routine use.

Application to tablet analysis : The proposed methods were successfully applied to determine atenolol in tablets without any coated colour lest it should interfere with the spectrophotometric method. The results are summarized in Table 2. The same batch tablets were analysed by the official Indian Pharmacopoeial method[2] for comparision. The results obtained by the proposed methods agreed well with those of the official method and with the label claim.

The results were compared statically by a Student's *t*-test for accuracy and a variance ratio *F*-test for precision with the official method at the 95% confidence level with four degrees of freedom as

Table 1 – Evaluation of accuracy and precision.

Method	Atenolol taken (mg)	Atenolol found (mg)	Range, (mg)	Standard deviation (mg)	Confidence limits**
VTM	5.0	4.96	0.26	0.15	4.96±0.14
	10.0	10.21	0.39	0.18	10.21±0.17
	15.0	14.86	0.40	0.17	14.86±0.16
PMM	20.0	20.55	1.60	0.54	20.55±0.77
	40.0	41.55	1.06	0.65	41.55±0.93
	60.0	61.52	2.66	0.99	61.52±1.41
CTM	20.0	21.04	2.66	0.99	21.04±1.41
	40.0	41.55	8.00	2.71	41.55±3.26
	60.0	62.85	8.00	2.72	62.85±3.87
SPM*	62.5	62.60	20.00	0.71	62.60±0.66
	125.0	129.80	16.90	0.63	129.80±0.58
	250.0	254.70	8.40	0.28	254.70±0.26

* In SPM, amount taken / found, range and standard deviation are in μg ml^{-1}

** At 95 % confidence level for six degrees of freedom in methods VTM & SPM, and four degrees of freedom for PMM and CTM.

Table 2 – Results of assay of tablets containing atenolol by the proposed methods

Tablet brand name**	Nominal brand amount (mg)	% Found* ±SD				
		VTM	PMM	CTM	SPM	Official method
		99.42±1.26	101.86±1.76	102.65±2.64	100.66±0.96	
Telol[a]	50	t=2.13	t=0.77	t=0.77	t=1.01	101.23±0.81
		F=2.42	F=4.72	F=4.72	F=1.40	
Betacard[b]	50	101.24±0.85	100.96±2.14	103.18±3.74	101.38±1.20	
		t=2.35	t=1.16	t=2.21	t=2.16	99.75±1.16
		F=1.86	F=3.40	F=10.40	F=1.07	
Atecard[c]	100	102.86±1.44	103.16±1.23	101.76±4.16	101.74±1.46	102.36±1.52
		t=0.53	t=0.92	t=0.33	t=0.66	
		F=1.11	F=1.53	F=7.49	F=1.08	
Aten[d]	100	97.85±0.72	98.14±1.65	98.76±3.68	99.38±0.88	99.36±1.16
		t=2.53	t=1.37	t=0.40	t=0.03	
		F=2.60	F=2.02	F=10.06	F=1.74	

* Mean value of five determinations

**Marketed by : a. Max India Ltd., b. Torrent Pharmaceuticals, c. Dobour Pharmaceuticals Ltd., * d. Kopran Ltd.

Tabulated *t*-value at 95% confidence level is 2.77

Tabulated *F*-value at 9% confidence level is 6.39

summarized in Table 2. The results showed that the calculated t – and F – values were less than the tabulated values indicating that no significant differences existed between the proposed and official methods in respect of accuracy and precision. Conductometric method was found to be less precise when compared to the other methods and the official method.

To establish the validity of the methods further, recovery tests were performed *via* standard addition technique. To a fixed amount of the drug in the tablet powder (pre-analysed), pure drug was added at three levels, and the total was found by the proposed methods. Each test was repeated three times. The recovery of added pure drug to tablet powder ranged from to 97.39 to 104.78 % inferring that commonly encountered tablet excipients and additives such as talc, starch, lactose, sodium alginate, magnesium stearate, calcium gluconate, calcium dihydrogenorthophosphate and cellulose did not interfere with the methods.

Conclusions

The methods described which are based on the neutralization reaction are simple, fairly rapid, relatively specific and reasonably accurate and precise for the determination of atenolol. Visual titrimetry which is applicable over a long linear range (2-20 mg) is more accurate and precise than the other three methods. Spectrophotometry employs mild working conditions without heating or extraction and involves the least number of experimental variables which quite often affect the validity of results. The method is more sensitive than many of the visible spectrophotometric, HPLC and GLC methods reported previously. These advantages coupled with the use of inexpensive chemicals and instruments make the methods highly suitable for routine quality control.

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Synthesis spectroscopic (IR, UV-visible and ESR) and magnetic studies of mixed ligand monochloro complexes of copper (II) containing Schiff base and benzimidazole moieties

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Abstract

Monochloro complex of copper(II) of the type $[(\mu\text{-Cl})_2 Cu_2 \{\eta^2 - (OPBZ)\}_2]$ (I) (where η2 = Number of connectivity sites involved in bonding the metal, OPBZ = {2-(o-hydroxyphenyl)} - benzimidazole) has been synthesized by the interaction of an aqueous ethanolic solution of copper (II) chloride (hydrated) with hot ethanolic solution of {2-(o-hydroxyphenyl)} – benzimidazole in desired molar ratio. Chloride replacement reaction in the chloro complex has led to the formation of hydrocarbon soluble mixed ligand complex of the type $[(\eta^2 - SMAB)\ Cu\ \{\eta^2 - (OPBZ)\}]$ (II) (where SMAB = salicylidene-2-methyl-1-aminobenzene). This monochloro complex and mixed ligand complex of Cu(II) have been characterised by IR, Electronic, ESR and Magnetic susceptibility measurements.

(**Keywords** : spectroscopic studies/ESR/Schiff base/benzimidazole/copper (II) complexes).

Introduction

Recent years have witnessed a great deal of interest in the synthesis and characterisation of transition metal chelates of benzimidazole derivatives. Among these derivatives, 2-(o-hydroxyphenyl)-benzimidazole is remarkable ligand due to its importance in biological, pharmacological, clinical and analytical applications[1-3]. A literature search reveals that work on these complexes are limited only upto bis-and tris-complexes with the corresponding divalent or trivalent metals. Benzimidazole and its related ligands act as a potential ligand for the preparation of various types of transition metal complexes due to their varying strong chelating behaviour towards metal ions. These are well known for their excellent medicinal properties and biological activities[4-6]. A limited attention[7-11] has been paid to the chemistry of monochloro complexes of later '3d' transition metals containing benzimidazole moieties, possibly due to their insoluble non-volatile and polymeric nature. In view of the above facts, we report herein, the synthesis, reactions and characterisation of some new monochloro complexes of copper(II), which have proved to be useful precursors for the synthesis of new and novel class of hydrocarbon soluble mixed ligand complexes.

Materials and Method

All chemicals of A.R. grade were used in the present investigations. Quantitative analysis of copper present in the complexes were carried out by atomic absorption spectroscopy, GBC-932 AA. IR spectra (4000-2000 cm^{-1}) were recorded on Perkin Elmer 1000 FTIR spectrometer in nujol-mull. Electronic spectra of the compounds were recorded in benzene and/or tetrahydrofuran on a Hitachi-220 spectrophotometer. Magnetic susceptibility[12,13] was measured on a Gouy balance using $Hg[Co(CNS)_4]$ as calibrating agent. ESR spectra of copper(II) complexes were recorded at room temperature on a E-112 ESR spectrometer.

Preparation of Ligands : The ligands {2-(o-hydroxyphenyl)} – benzimidazole, (HOPBZ) and Schiff base, Salicylidene – 2 – methyl – 1 – amino-benzene, (SMAB) have been prepared by established method[14,15].

O-phenylene diamine + salicylamide

Δ | $-H_2O + NH_3$

2-(O-hydroxyphenyl)-benzimidazole (HOPBZ)

(HOPBZ) + $CuCl_2 . 2H_2O$ (aqEtOH)

Sodium acetate solution digested ~ 8h

[(Cl) Cu(OPBZ)] . XH_2O (Light Brown)

Dried at ~100°C under vacuo

[(Cl) Cu(OPBZ)] [I]
(Brown solid)

MeOH Δ | $-H_2O$

Salicylidene-2-methyl-1-aminobenzene (SMAB)

Na (metal) (dry EtOH)

Na (SMAB)

THF/benzene | Δ ~4h, – NaCl

[(SMAB) Cu(OPBZ)] . X THF (Light Brown)

Dried at ~40°–50°C under vacuo

[(SMAB) Cu(OPBZ)] [II]
(Green solid)

(Square planar) ⇌ THF solvent **(Distorted Octahedral)**

Scheme I – Synthesis of Copper(II) Complexes (I) and (II)

Preparation of Complexes

(A) *Monochloro {2-(o-hydroxyphenyl)} - Benzimidazolato-copper (II); [(μ–Cl)$_2$ Cu$_2$ {η^2 – (OPBZ)$_2$] (1).*

An aqueous ethanolic solution (50% ethanol, ~50 cm^3) of copper (II) chloride (2.433g, 14.3 mmol) was added dropwise to a stirred hot ethanol (~75 cm^3) solution containing 2-(o-hydroxyphenyl)-benzimidazole (3g, 14.3 mmol), which yielded as a pale yellow coloured precipitate. Further, dropwise addition of dilute solution of sodium acetate with continuous stirring afforded dense light brown coloured precipitate from initial pale yellow colour. After complete precipitation, it was digested on water bath for ~1h. The complex so obtained was filtered, washed thrice with aqueous ethanol and dried at 100°C under reduced pressure to obtain [(μ–Cl)$_2$ Cu$_2$ {η^2 – (OPBZ)$_2$] (I) brown powdered solid. (4.000g 91%). The product on analysis was found to have Cu, 20.10%, Cl, 12.0% and (Cald) for Cu (20.60%), Cl (11.51%).

(B) Copper (II) complex containing {2-(o-hydroxyphenyl)} - benzimidazole and salicylidene-2-methyl-1-aminobenzene moieties [(η^2-SMAB) Cu {η^2-(OPBZ)}] (II)

To a stirred hot brown suspension of monochloro {2-(o-hydroxyphenyl)}-benzimidazolato-copper(II) (0.300 g, 0.97 mmol) complex in tetrahydrofuran (~30 cm^3), was added sodium salt of salicylidene-2-methyl-1-aminobenzene (0.230 g, 0.97 mmol) in 1:1 stoichiometric ratio. The reaction mixture was allowed to reflux for ~1 h, during which the colour of the solution changed from brown to green. The precipitated NaCl (0.057 g, 0.97 mmol) was removed by filtration. The solvent was removed from the filtrate under reduced pressure to afford [(η^2-SMAB) Cu {η^2-(OPBZ)}] (II) (Scheme-I), which was purified by recrystallization from a benzene/THF mixture to give green powdered solid (0.380g. 81%). Analysis of the title derivative was found to be Cu 12.9% and (Calcd) for Cu (13.17%).

Results and Discussion

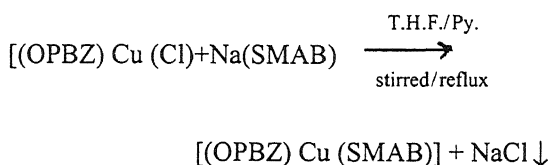
Synthesis and some physical properties of [(μ-Cl)$_2$ Cu$_2$ {η^2-(OPBZ)}$_2$] (I) :

A hot ethanolic solution of {2-(o-hydroxyphenyl)}-benzimidazole; (HOPBZ) was added to an aqueous ethanolic solution of copper (II) chloride (hydrated) in equimolar ratio, a pale yellow coloured precipitate was obtained. Further addition of sodium acetate afforded dense brown colour product [(μ-Cl)$_2$ Cu$_2$ {η^2-(OPBZ)}$_2$] (I).

The obtained product (I) was digested, filtered, washed with aqueous ethanol, and finally dried at ~100°C under reduced pressure.

Attempts have been made to purify the complex using a number of solvents such as benzene, isopropanol, ethanol etc. However, it has been realised that the complex is highly insoluble in most of the common solvents and mixture of solvents. The complex has tendency to form adducts, when treated with THF/pyridine. Due to insolubility in the non-polar solvents, the molecular weight determination could not be made possible either by cryoscopically or by ebullioscopically, though it is expected to be polymeric in nature.

Attempts have been made during the course of present investigation to prepare soluble complex by the interaction of sodium salt of Schiff base; which could throw light on structure of copper (II) complex. The reactions of chloro complex of copper(II) containing benzimidazole moiety with sodium salt of salicylidene-2-methyl-1-aminobenzene, Na(SMAB) in the equimolar ratio, in the presence of mixture of THF/pyridine, which can be represented as follow:

$$[(OPBZ)\ Cu\ (Cl) + Na(SMAB) \xrightarrow[\text{stirred/reflux}]{\text{T.H.F./Py.}} [(OPBZ)\ Cu\ (SMAB)] + NaCl\downarrow$$

This mixed ligand complex is coloured solid and found to be soluble in common organic solvents like benzene, n-hexane etc. and has been purified by recrystallization in the mixture of solvents such as THF and benzene.

Infrared spectral studies : The N-H stretching frequency ν_{N-H} observed in the spectra of the ligand 2-(o-hydroxyphenyl)-benzimidazole (HOPBZ) at ~3200 cm^{-1} remain almost unchanged in the complex

containing benzimidazole moiety[16], indicating non-participation of N-H group. The monochloro complex $[(\mu\text{-Cl})_2 Cu_2 \{\eta^2\text{-(OPBZ)}\}_2]$ (I) exhibit characteristic IR frequencies at 280(s) cm^{-1} and has been assigned for $\nu_{Cu\text{-}Cl}$ bridging vibration[17], suggesting bridging of chlorine between two copper (II) centers.

The IR spectra of the ligands (SMAB and HOBZ) showed bands at 1647-1618 cm^{-1} characteristics for $\nu_{C=N}$, whereas bands shifted to lower frequency region at 1604-1595 cm^{-1} in complexes $[(\mu\text{-Cl})_2 Cu_2 \{\eta_2\text{-(OPBZ)}\}_2]$ (I) and $[(\eta_2\text{-SMAB}) Cu \{\eta^2\text{-(OPBZ)}\}]$ (II) suggeting coordination through hetero nitrogen atom of azomethine[18] group. The IR frequencies of ν(C-O) ·(phenolic) in the ligands are generally observed in the region 1256-1248 cm^{-1}, which get shifted towards higher region 1283-1267 cm^{-1}, thereby indicating that bonding takes place through phenolic oxygen[19] (after deprotonation of phenolic OH group of the ligands).

The medium to strong intensity bands in the region (237(m)-234(s) cm^{-1}) and (580(s) - 559(m) cm^{-1}) in complexes have been assigned to $\nu_{Cu\text{-}N}$ and $\nu_{Cu\text{-}O}$ mode respectively[17,20].

Electronic spectral studies : The visible spectra of complexes $[(\mu\text{-Cl})_2 Cu_2 \{\eta^2\text{-(OPBZ)}\}_2]$ (I) and $[\eta^2\text{-SMAB}) Cu(\eta^2\text{-OPBZ})]$ (II) have been recorded in pyridine/THF mixture which exhibits broad asymmetric band at ~14903 and ~15673 cm^{-1} respectively attributed to ${}^2E_g \rightarrow {}^2T_{2g}$ transition, due to Jahn-Teller distortion in d^9 (Cu^{2+}) systems as well as due to the presence of electrogenative 'N' and 'O' donor atoms causes the broadening of the absorption band, suggesting a distorted octahedral geometry (in D_{4h} symmetry) for copper(II) complexes[21,22]. Besides above bands additional intense bands have been observed at ~26882 cm^{-1} assigned as ligand to metal charge transfer band (L$\rightarrow$M, CT) and at ~33445 cm^{-1} assigned to intraligand charge transfer band[23,24].

ESR spectral studies : The ESR spectrum of monochloro {2-(o-hydroxyphenyl)-benzimidazolato}-copper (II) [I] in polycrystalline solid state at room temperature has been measured.

ESR spectrum indicates $g_{||} > g_{\perp} > 2.02$ in $d_{x^2-y^2}$ (or d_{xy}) state, whilst a d_{z^2} ground state term usually gives a spectrum with $g_{\perp} > g_{||} \cong 2.00$. Copper (II) system studied herein, shows a pronounced peak for which $g_{||} \cong 2.32$. In an axial symmetry, the g values are related by the expression $G = (g_{||}-2)/(g_{\perp}-2)$, which measures the exchange interaction between copper centres in polycrystalline solid.[25] If $G > 4$, exchange interaction is negligible; values of $G < 4$ indicates considerable exchange interaction in the solid complex. The g_{av} values have been calcu-lated according to the relation, $g_{av} = 1/3(g_{||} + 2g_{\perp})$ and gave values in the range 2.17 ± 0.03, which are in aggrement with an orbitally non-degenerate ground state. It appears that g value obtained corresponds to molecular g value, which are characteristics of square planar geometry around copper(II), obtained as a result of coordination through nitrogen atom. These have been corroborated by IR and electronic spectral studies.

Magnetic studies : The copper(II) complex of $3d^9$ configurations exhibits paramagnetism corresponding to one unpaired spin (S=1/2, $\mu_{S.O.}$=1.73BM). However, magnetic moment is usually observed to be slightly higher ~2.0BM. Copper(II) complexes usually have a distorted octahedral stereochemistry, although a few are known to be square planar approaching towards a tetrahedral stereochemistry[26]. The observed magnetic moment at room temperature for monochloro-{2-(o-hydroxyphenyl)-benzimidazolato}-copper(II) is 2.36BM which is in agreement with reported values (1.8-2.4BM) for Cu(II) d^9 system.

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Speciation studies of nickel(II) complexes of L-glutamine and succinic acid in urea-water mixtures

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Abstract

Speciation of Ni^{II} complexes of glutamine (Gln) and succinic acid (Suc) in 0.0-36.83%, w/v urea-water mixtures at an ionic strength of 0.16 mol dm^{-3} and temperature 303K has been investigated pH metrically. The species detected for Gln complexes are ML, ML_2 and ML_3H and those for Suc are MLH, ML_2H and ML_3H. The decreased stability of the complexes with increased urea content is due to the electrostatic forces and denaturing power and complexing ability of urea. The species distribution and the plausible equilibria for the formation of the species are also presented.

(**Keywords :** complex equilibria/speciation/L-glutamine/succinic acid/nickel)

Introduction

L-Glutamine (Gln) and succinic acid (Suc) are biologically important[1] ligands. Hence, the protonation equilibria of Gln and Suc in urea-water[2], dimethylformamide-water[2], ethylene glycol-water[3] and acetonitrile-water[4] mixtures were studied. Similarly, their stability constants with Ca^{II} and Mg^{II} were determined in ethylene glycol-water[3] and in acetonitrile-water mixtures[3]. No such studies were found for Ni(II) complexes in the literature. Hence, the speciation studies of Gln and Suc with Ni^{II} in urea-water mixtures have been reported in this paper.

Materials and Method

Solutions of L-glutamine, succinic acid and nickel(II) chloride (E. Merck) were prepared in triple distilled water. A 99.5% pure urea (E. Merck) was used without further purification. To assess the errors that might have crept into the determination of the concentration, the data were subjected to ANOVA[6]. The strength of alkali was determined using the Gran plot method[7]. Alkalimetric titrations with different ratios (1:2 and 1:3) of metal-to-ligand were carried out in the medium containing varying concentrations (0.0 – 36.83% w/v) of urea in water at an ionic strength of 0.16 mol dm^{-3} with NaCl at 303.0 ± 0.1 K using a Systronics 335 pH meter. The glass electrode was equilibrated in urea-water mixture containing inert electrolyte. The correction factor ($\log F$), to correct the pH meter dial reading, was determined using the computer program SCPHD[8]. Other experimental details are given elsewhere[6]. The approximate complex stability constants were calculated using the computer program SCPHD. By following some heuristics[9] in the refinement of the stability constants, the best-fit chemical models for each system were arrived at using the computer program MINIQUAD75[10].

Results and Discussion

The amino and carboxyl groups of L-glutamine and the two carboxyl groups of succinic acid are protonated. Alkalimetric titration curves in urea-water mixtures revealed that the acido-basic equilibria of L-glutamine and succinic acid were active in the pH ranges 1.5 – 9.0 and 2.5 – 7.0, respectively[2]. The present study is confined to the pH ranges 2.5 – 8.5 and 2.5 – 5.5 for Ni-Gln and Ni-Suc, respectively. Based on the active forms of the ligands in these pH ranges, models containing various numbers and combination of complex species of Ni^{II} with Gln and Suc are generated using an expert system package CEES[11]. These models are inputted to MINIQUAD75 along with the alkalimetric titration data. The best-fit model is selected using the statistical parameters[12] of the least squares residuals. The finally refined model for Gln complexes contains ML, ML_2 and ML_3H and that for Suc contains MLH, ML_2H and ML_3H species. The final models are given in Table 1, along with the statistical parameters. The

Table 1 – Best-fit chemical models of Ni^{II} complexes of L-glutamine and succinic acid in urea-water mixtures. No. of titrations in each percentage = 4, Temperature = 303K, Ionic strength = 0.16 mol. dm^{-3}

%w/v	log β_{mlh} (SD)			NP	U_{corr} x10^6	χ^2	Skew-ness	Kurto-sis	R-factor
	110	120	131						
			L-Glutamine complexes (pH range : 2.5 – 8.5)						
5.80	4.87(5)	9.11(4)	19.09(3)	37	2.18	115.38	0.20	3.35	0.052
11.52	4.77(3)	8.64(3)	18.83(7)	43	3.68	76.34	0.18	3.86	0.063
20.31	4.74(2)	8.94(1)	18.64(4)	36	3.53	35.56	0.10	5.19	0.023
29.64	4.45(1)	8.16(1)	18.44(5)	32	7.44	49.17	–0.06	3.97	0.038
36.83	4.22(2)	7.51(1)	18.29(8)	36	3.53	23.26	0.07	4.98	0.023
	111	121	131						
			Succinic acid complexes (pH range : 2.5 – 5.5)						
5.82	7.92(3)	9.88(3)	12.24(4)	59	4.29	83.20	0.00	3.19	0.049
11.52	7.26(3)	9.33(4)	12.11(3)	64	2.22	107.25	–1.09	6.42	0.035
20.31	6.45(9)	8.63(7)	11.40(9)	60	1.13	54.22	–0.50	3.65	0.026
29.64	6.22(4)	7.73(6)	10.69(2)	40	8.73	41.33	1.02	5.72	0.036
36.83	6.16(3)	7.10(4)	9.90(7)	64	2.12	66.83	–0.98	6.16	0.038

closeness of skewness to zero and kurtosis to three indicates that the residuals follow Gaussian distribution and so least squares technique can be applied. The low standa-d deviation in the model parameters (logβs) illustrate the adequacy of the models.

Perusal of the models indicates that only protonated species are present under the acidic pH (2.5 to 5.5) conditions for Ni(II)-Suc systems. Above a pH of 5.5, precipitation was observed during the alkalimetric titrations, may be due to the hydrolysis of the complexes. This is possible since Suc is a weak ligand. On the other hand both protonated and unprotonated (Ni(II)-Gln complexes were refined in the pH range (2.5 to 8.5), inferring the stability of these complexes even in slightly alkaline pH. This comparison infers that Gln (N, O – donor) is a stronger ligand than Suc (O, O – donor).

Solute-solvent interactions : The linear variation (Fig. 1) of stability constants of Gln and Suc complexes of Ni^{II} in urea-water mixtures with $1/D$ (where D is dielectric constant of the medium)

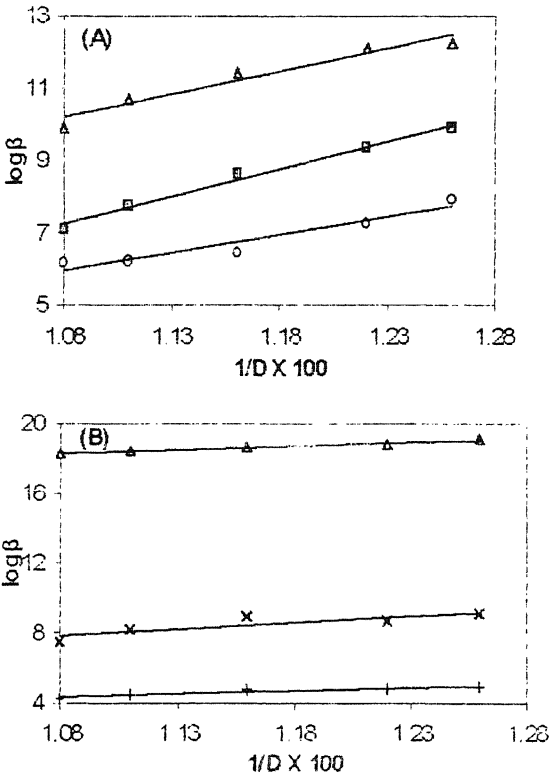



Fig. 1 – Variation of logβ with reciprocal of dielectric constant of urea-water mixtures (A)Ni(II)-Suc, (B)Ni(II)-Gln; (o) $\log\beta_{111}$, (D) $\log\beta_{131}$, (D) $\log\beta_{121}$, (+) $\log\beta_{110}$ and (x) $\log\beta_{120}$.

indicates that electrostatic forces dominate[13] the equilibrium process under the present experimental conditions. Urea acts as a denaturant of macromolecules by interacting with peptide groups through its amido group and by breaking the water structure[14]. In the same way urea also interacts with amino acids there by decreasing the chelating power of the ligands. In addition, urea competes with the ligands for complexation with the metals. Hence, the stability of the species decreased with increasing urea content. Urea also increases the dielectric constant of the medium, which also unfavours the formation of the complex.

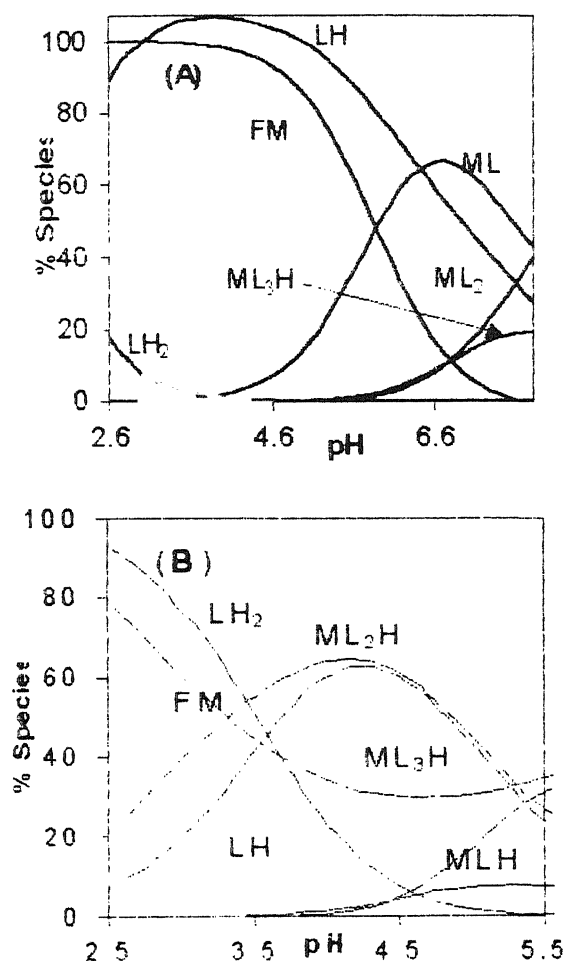



Fig. 2 – Species distribution diagrams in 5.8% w/v urea-water mixture : (A) Ni(II)-Gln. and (B) (Ni(II)-Suc.

Distribution diagrams : The variation of species concentration with pH is shown in Fig. 2 for typical systems. In both the succinic acid and L-glutamine cases, species concentrations decreased with increasing urea content. The ML_3H species has the maximum concentration at higher pH. The concentration of free metal ion is more in the presence of Suc (Fig. 2B) than in the presence of Gln (Fig. 2A). This also supports the statement "succinic acid is a weaker ligand than glutamine". The formation equilibria, based on the above observations, are represented below. The charges of the species are omitted for clarity.

(a) $M(II) + LH_2 \longleftrightarrow MLH + H^+$

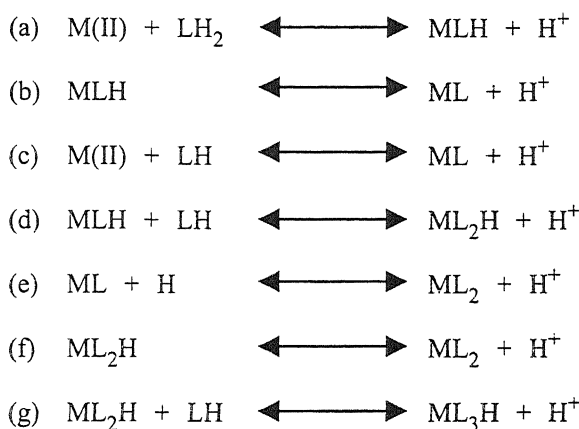
(b) $MLH \longleftrightarrow ML + H^+$

(c) $M(II) + LH \longleftrightarrow ML + H^+$

(d) $MLH + LH \longleftrightarrow ML_2H + H^+$

(e) $ML + H \longleftrightarrow ML_2 + H^+$

(f) $ML_2H \longleftrightarrow ML_2 + H^+$

(g) $ML_2H + LH \longleftrightarrow ML_3H + H^+$

The formation of ML species may be due to either or both the equilibria (b) and (c). Similarly the ML_2 species is formed through the equilibria (e) and (f).

Conclusions

1. The biomimetic studies of Ni(II) complexes with L-glutamine and succinic acid indicate that all the succinic acid complexes are protonated (MLH, ML_2H and ML_3H) under acidic pH (2.5 – 5.5) conditions. These complexes decompose and metal hydroxides are formed in alkaline pH conditions.

2. L-glutamine forms both protonated and unprotonated complexes (ML, ML_2 and ML_3H) in the pH range (2.5 – 8.5). Even in slightly alkaline pH, these complexes are not decomposed because glutamine is stronger complexing agent than succinic acid.

3. Urea acts as denaturant and structure breaker of water and increases the dielectric constant of the medium. It also competes with the ligands for complexation with the metals. As a cumulative effect the stabilities of the complexes have decreased with increased urea content.

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On p-th order of a function analytic in the unit disc

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Abstract

This paper is concerned with the study of the maximum modulus and the coefficients of the power series expansion of a function analytic in the unit disc.

(**Keywords** : analytic function/unit disc/p-th order/lower p-th order)

Introduction, Definitions and Notations

Let $f(x) = \sum_{n=0}^{\infty} c_n z^n$ be analytic in $U = \{z: |z| < 1\}$ and $M(r) = M(r, f)$ be the maximum of $|f(z)|$ on $|z| = r$. In a paper Sons[1] defined the order ρ and lower order λ as

$$\begin{matrix}\rho \\ \lambda\end{matrix} = \lim_{r \to 1} \begin{matrix}\sup \\ \inf\end{matrix} \frac{\log \log M(r)}{-\log(1-r)}.$$

The following results give the characterization of order and lower order of a function f analytic in U, in terms of the co-efficients c_n.

Theorem 1[2] *{p-47}* : Let $f(z) = \sum_{n=0}^{\infty} c_n z^n$ be analytic in U and have order $\rho (0 \le \rho \le \infty)$. Then

$$\frac{\rho}{1+\rho} = \limsup_{n \to \infty} \frac{\log^+ \log^+ |c_n|}{\log n}.$$

Theorem 2[3] : Let $f(z) = \sum_{n=0}^{\infty} c_n z^n$ be analytic in U, having lower order $\lambda (0 \le \lambda \le \infty)$. Then

$$\frac{\lambda}{1+\lambda} = \liminf_{n \to \infty} \frac{\log^+ \log^+ |c_n|}{\log n}$$

We use the following notations.

Notation 1[4] : $\log^{[0]} x = x$, $\exp^{[0]} x = x$ and for positive integer m, $\log^{[m]} x = \log(\log^{[m-1]} x)$, $\exp^{[m]} x = \exp(\exp^{[m-1]} x)$.

Notation 2 : For $0<x<\infty$ we write $\log^{*(01)} x = x$, $\log^{*(1)} x = \log(1+x)$, $\log^{*(2)} x = \log(1+\log(1+x))$ $\log^{*(3)} x = \log(1+\log(1+\log(1+x)))$ etc.

Definition[5] : If $f(z) = \sum_{n=0}^{\infty} c_n z^n$ be analytic in U, its p-th order ρ_p and lower p-th order λ_p are defined as

$$\begin{matrix}\rho_p \\ \lambda_p\end{matrix} = \lim_{r \to 1} \begin{matrix}\sup \\ \inf\end{matrix} \frac{\log^{[p]} M(r)}{-\log(1-r)}, p \ge 2.$$

The purpose of this paper is to generalise the above results for p-th order and lower p-th order.

From here onwards $f(z) = \sum_{n=0}^{\infty} c_n z^n$ will denote a function analytic in unit disc U.

Lemmas and Theorems

Theorem 3 : Let $f(z)$ be analytic in U and have p-th order $\rho_p (0 \le \rho_p \le \infty)$. Then

$$\frac{\rho_p}{1+\rho_p} = \limsup_{n \to \infty} \frac{\log^{+[p]} |c_n|}{\log n}. \quad (1)$$

We first prove the following lemmas.

Lemma 1 : Let the maximum modulus $M(r)$ of a function $f(z)$, analytic in U, satisfy

$$\log^{[p-1]}M(r)<A(1-r)^{-B},\ 0< A,\ B < \infty \qquad (2)$$

for all r such there shall that $r_0\ (A,B) < r < 1$. Then for all $n > n_0\ (A,B)$,

$$\log^{[p-1]}|c_n| \le S(A,B)\, n^{B/(B+1)}$$

where, $S(A,B) = (1+2B)\left(\dfrac{A}{B^B}\right)^{\frac{1}{B+1}}$.

Proof : Define a sequence $\{r_n\}$ by

$$(1-r_n)^{-1} = (n/AB)^{\frac{1}{B+1}}$$

Then $r_n \to 1$ as $n \to \infty$. By Cauchy's inequality and (2) we have for all $n>n_0\ (A,B)$ $\log|c_n| < \log M(r_n) - n\log r_n$.

$$< \exp^{[p-2]}\left\{A(1-r_n)^{-B}\right\} + n(1-r_n)\left[1+0(1)\right]$$

$$= \exp^{[p-2]}\left\{A\left(\frac{n}{AB}\right)^{\frac{B}{B+1}}\right\} + n\left(\frac{AB}{n}\right)^{\frac{1}{B+1}}\left[1+0(1)\right]$$

$$\le \left[1+B\{1+0(1)\}\right]\exp^{[p-2]}\left\{A\left(\frac{n}{AB}\right)^{\frac{B}{B+1}}\right\}$$

$$\le \exp^{[p-2]}\left\{(1+2B)A\left(\frac{n}{AB}\right)^{\frac{B}{B+1}}\right\}.$$

$$\therefore\quad \log^{[p-1]}|c_n| \le S(A,B)\, n^{\frac{B}{B+1}}$$

where $S(A,B) = (1+2B)\left(\dfrac{A}{B^B}\right)^{\frac{1}{B+1}}$.

Lemma 2 : Let $f(z)$ be analytic in U and satisfy $\log^{[p-1]}|c_n| < C\,n^D,\ 0<C<\infty, 0<D<1$, for all $n>n_0\ (C,D)$. Then for all r such that $r_0\ (C,D)<r<1$ $\log^{[p-1]} M(r) < T(C,D)\left(\log(1/r)\right)^{-D/(1-D)}$ where $T(C,D)=C^{1/(1-D)}\ D^{D/(1-D)}\ [1+0(1)]$.

Proof : For all $n>n_0(C,D)$, $|c_n|<\exp^{[p-1]}(C\,n^D)$.

Now for $|z|=r<1$

$$M(r) < \sum_{n=0}^{\infty}|c_n|\,r^n < K(n_0) + \sum_{n=n_0+1}^{\infty}\exp^{[p-1]}\left(cn^{\frac{B}{B+1}}\right)r^n,$$

where $B = \dfrac{D}{1-D}$.

Choose $$N = N(r) = \left[\left(\frac{2^{2p-3}.C}{\log^{*(p-2)}\left(\log\frac{1}{r}\right)}\right)^{B+1}\right]$$

Where $[x]$ denotes the greatest integer not greater than x.

Clearly $N(r)\to\infty$ as $r\to 1$.

The above estimate of $M(r)$, for all r sufficiently close to 1, gives.

$$M(r) < K(n_0) + N(r)\,H(r) + \sum_{n=N+1}^{\infty} r^{\frac{n}{2}} \qquad (3)$$

where

$$H(r) = \max_n\left\{\exp^{[p-1]}\left(cn^{\frac{B}{B+1}}\right)r^n\right\};$$

for if $n \ge N+1$, then

$$n > \left(\frac{2^{2p-3}C}{\log^{*(p-2)}\left(\log\frac{1}{r}\right)}\right)^{B+1}$$

$$\therefore\quad Cn^{\frac{B}{B+1}} < \frac{n}{2^{2p-3}}\log^{*(p-2)}\left(\log\frac{1}{r}\right)$$

$$= \log\left[1+\log^{*(p-3)}\left(\log\frac{1}{r}\right)\right]^{\frac{n}{2^{2p-3}}}$$

$$\leq \log\left[1+\frac{n}{2^{2p-4}}\log^{*(p-3)}\left(\log\frac{1}{r}\right)\right].$$

$$\therefore \quad \exp\left(Cn^{\frac{B}{B+1}}\right) \leq 1+\frac{n}{2^{2p-4}}\log^{*(p-3)}\left(\log\frac{1}{r}\right)$$

$$\leq \frac{n}{2^{2p-5}} \log^{*(p-3)}\left(\log\frac{1}{r}\right)$$

$$\leq \log\left[1+\frac{n}{2^{2p-6}}\log^{*(p-4)}\left(\log\frac{1}{r}\right)\right].$$

$$\therefore \quad \exp^{[2]}\left(Cn^{\frac{B}{B+1}}\right) \leq 1+\frac{n}{2^{2p-6}}\log^{*(p-4)}\left(\log\frac{1}{r}\right)$$

$$\leq \frac{n}{2^{2p-7}} \log^{*(p-4)}\left(\log\frac{1}{r}\right).$$

Taking repeated exponential, we obtain

$$\exp^{[p-2]}\left(Cn^{\frac{B}{B+1}}\right) < \frac{n}{2}\log\frac{1}{r}.$$

$$\therefore \quad \exp^{[p-1]}\left(Cn^{\frac{B}{B+1}}\right) r^n < r^{\frac{n}{2}}.$$

The infinite series in (3) is bounded by $r^{\frac{N+1}{2}}\left(\dfrac{1}{1-r^{\frac{1}{2}}}\right)$. Since $B>0$, we have

$$-\frac{N+1}{2}\log\frac{1}{r}-\log\left(1-r^{\frac{1}{2}}\right) < -\frac{1}{2}\left(\frac{2^{2p-3}.C}{\log^{*(p-2)}\left(\log\frac{1}{r}\right)}\right)^{B+1}$$

$$\log\frac{1}{r}-\log(1-r)+\log\left(1+r^{\frac{1}{2}}\right)$$

$$< -\frac{1}{2}\left(\frac{2^{2p-3}.C}{\log\frac{1}{r}}\right)^{B+1} .\log\frac{1}{r}-\log(1-r)+\log\left(1+r^{\frac{1}{2}}\right)$$

$\rightarrow -\infty$ as $r \rightarrow 1$.

Thus for r sufficiently close to 1,

$$\sum_{n=N+1}^{\infty} r^{\frac{n}{2}} = 0(1). \tag{4}$$

The maximum of $\exp^{[p-1]}\left(Cn^{\frac{B}{B+1}}\right) r^n$ assumed at the point $\left(\dfrac{BC}{(B+1)\log\frac{1}{r}}\right)^{B+1}$ and $H(r)$ is given by

$$\log H(r) = \exp^{[p-2]}\left(Cn^{\frac{B}{B+1}}\right) + n \log r$$

$$= \exp^{[p-2]}\left\{\frac{C B^B . C^B}{(B+1)^B\left(\log\frac{1}{r}\right)^B}\right\} - \frac{(BC)^{B+1}}{(B+1)^{B+1}.\left(\log\frac{1}{r}\right)^{B+1}}.\log\frac{1}{r}$$

$$< \exp^{[p-2]}\left\{\frac{C^{B+1}.B^B}{(B+1)^B\left(\log\frac{1}{r}\right)^B}\right\}. \tag{5}$$

In view of (4) and (5), inequality (3), for all r such that r_0 $(C, D) < r < 1$, becomes

$$\log M(r) < -(B+1)\log^{[p]}\frac{1}{r} + \exp^{[p-2]}\left\{\frac{C^{B+1}.B^B}{(B+1)^B\left(\log\frac{1}{r}\right)^B}\right\} + o(1)$$

$$< \exp^{[p-2]}\left\{\frac{C^{B+1}.B^B}{(B+1)^B\left(\log\frac{1}{r}\right)^B}\right\}[1+o(1)].$$

$$\therefore \ \log^{[p-1]} M(r) < \frac{C^{B+1} B^B}{(B+1)^B} \left[1+o(1)\right] \left(\log\frac{1}{r}\right)^{-B}$$

$$= C^{\frac{1}{1-D}} D^{\frac{D}{1-D}} \left[1+o(1)\right] \left(\log\frac{1}{r}\right)^{\frac{-D}{1-D}}$$

$$= T(C, D) \left(\log\frac{1}{r}\right)^{\frac{-D}{1-D}}$$

where $T(C, D) = C^{\frac{1}{1-D}} D^{\frac{D}{1-D}} \left[1+o(1)\right]$.

Proof of the Theorem 1 : If $|c_n|$ is bounded by K for all n, then $\sum_{n=0}^{\infty} |c_n| r^n$ is bounded by $\frac{K}{1-r}$.

$$\therefore \ M(r) \le \sum_{n=0}^{\infty} |c_n| r^n \le \frac{K}{1-r} < \exp^{[p-1]}\left(\frac{1}{1-r}\right)^{\varepsilon} \quad \text{for}$$

any $0<\varepsilon<1$ and r sufficiently close to 1.

$$\therefore \ \rho_p = \lim_{r\to 1} \sup \frac{\log^{[p]} M(r)}{-\log(1-r)} \le \varepsilon .$$

Since $0<\varepsilon<1$ is arbitrary, $\rho_p=0$ and so (1) is satisfied. Thus we need to consider only the case

$$\lim_{n\to\infty} \sup |c_n| = \infty.$$

In this case, all the $\log^+$ in (1) may be replaced by log.

First, let $0<\rho_p<\infty$ and $\rho'_p > \rho_p$. Then, for r sufficiently close to 1,

$$\log^{[p-1]} M(r) < (1-r)^{-\rho'_p}$$

Using Lemma 1, with $A = 1$, $B = \rho'_p$ it follows from the above inequality that for $n>no$ (ρ'_p)

$$\log^{[p-1]} |c_n| \le (1+2\rho'_p) \left(\frac{1}{\rho_p^{,\rho'_p}}\right)^{\frac{1}{\rho'_p+1}} . \ n^{\frac{\rho'_p}{\rho'_p+1}}$$

$$\therefore \quad \lim_{n\to\infty} \frac{\log^{[p]} |c_n|}{\log n} \le \frac{\rho'_p}{\rho'_p+1}$$

Since is arbitrary, it follows that

$$\lim_{n\to\infty} \sup \frac{\log^{[p]} |c_n|}{\log n} \le \frac{\rho_p}{1+\rho_p} . \tag{6}$$

Since f is analytic in U, the above inequality is trivially true if $\rho_p=\infty$ and the right hand side is interpreted as 1 in this case.

Conversely, if $\theta = \lim_{n\to\infty} \sup \frac{\log^{[p]} |c_n|}{\log n}$ then $0\le\theta\le 1$. First let $\theta<1$ and choose $\theta<\theta'<1$.

Then for all sufficiently large n.

$$\log^{[p-1]} |c_n| < n^{\theta'}$$

Using Lemma 2, with $C=1$, $D=\theta'$, it follows from the above inequality that for all r such that $r_0(\theta')<r<1$,

$$\log^{[p-1]} M(r) < \theta'^{\frac{\theta'}{1-\theta'}} \left(\log\frac{1}{r}\right)^{\frac{-\theta'}{(1-\theta')}} \left[1+o(1)\right]$$

$$\lim_{n\to\infty} \sup \frac{\log^{[p]} M(r)}{-\log(1-r)} \le \frac{\theta'}{1-\theta'} \lim_{r\to 1} \sup \frac{\log\frac{1}{r}}{-\log(1-r)}$$

$$\therefore \ \rho_p \le \frac{\theta'}{1-\theta'} .$$

Since $\theta'>\theta$ is abritrary, it follows that

$$\frac{\rho_p}{1+\rho_p} \le \theta = \lim_{n\to\infty} \sup \frac{\log^{[p]} |c_n|}{\log n} . \tag{7}$$

If $\theta=1$, the above inequality is obviously true.

Inequalities (6) and (7) together give (1) when $\lim_{n\to\infty} \sup |c_n| = \infty$.

Theorem 2 : Let $f(z)$ be analytic in U, having lower order $\lambda_p(0 \le \lambda_p \le \infty)$. Then

$$\frac{\lambda_p}{1+\lambda_p} \ge \liminf_{n \to \infty} \frac{\log^{+[p]} |c_n|}{\log n}.$$

Proof : Let $\liminf_{n \to \infty} \frac{\log^{+[p]} |c_n|}{\log n} = A. \qquad (8)$

First suppose that $0<A<1$. From (8), for $0<\varepsilon<A$,

$$\log |c_n| > \exp^{[p-2]} n^{A-\varepsilon}$$

for $n>N=N(\varepsilon)$. By Cauchy's estimate

$$\log M(r) \ge \log |c_n| + n \log r, \qquad (9)$$

Choose, $n = \left(\log \frac{1}{r}\right)^{\frac{1}{A-\varepsilon-1}}$

Then

$$\log M(r) > \exp^{[p-2]}\left(\log\frac{1}{r}\right)^{\frac{A-\varepsilon}{A-\varepsilon-1}} - \left(\log\frac{1}{r}\right)^{\frac{1}{A-\varepsilon-1}} \cdot \left(\log\frac{1}{r}\right)$$

$$> \frac{1}{2}\exp^{[p-2]}\left(\log\frac{1}{r}\right)^{\frac{A-\varepsilon}{A-\varepsilon-1}}$$

$$\log^{[p]} M(r) > \frac{A-\varepsilon}{A-\varepsilon-1}\log^{[2]}\frac{1}{r} + O(1)$$

$$\therefore \quad \frac{\log^{[p]} M(r)}{-\log(1-r)} > \frac{A-\varepsilon}{A-\varepsilon-1}\frac{\log^{[2]}\frac{1}{r}}{\log(1-r)} + o(1)$$

$$\therefore \quad \lambda_p = \liminf_{r \to 1} \frac{\log^{[p]} M(r)}{-\log(1-r)} \ge \frac{A-\varepsilon}{1-A+\varepsilon}.$$

Since $0<\varepsilon<A<1$ is arbitrary, $\lambda_p \ge \frac{A}{1-A}$.

Which implies $\frac{\lambda_p}{1+\lambda_p} \ge A.$

This inequality holds obviously when $A=0$. For $A=1$, the above arguments with a number K arbitrarily near to 1 in place of A-ε, give

$$\frac{\lambda_p}{1+\lambda_p} = 1.$$

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Relative Valiron defects of meromorphic functions

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Abstract

In the paper we compare the relative Valiron defect with the relative Nevanlinna defect of a meromorphic function.

(**Keywords** : relative Nevanlinna defect/relative Valiron defect/meromorphic function)

Introduction and Definition

Let f be a non-constant meromorphic function defined in the open complex plane c. For $\alpha \in c\cup\{\infty\}$ let $n(t, \alpha; f)$ denote the number of roots of $f=\alpha$ in $|z| \leq t$, the multiple roots being counted according to their multiplicities and $N(t, \alpha; f)$ is defined in the usual way in terms of $n(t, \alpha; f)$. Similarly, $\bar{n}(t, \alpha; f)$ denotes the number of distinct roots of $f=\alpha$ in $|z| \leq t$ and $\bar{N}(t, \alpha; f)$ is also defined in the usual way in terms of $\bar{n}(t, \alpha; f)$.

The Nevanlinna defect $\delta(\alpha; f)$ and the Valiron defect $\Delta(\alpha; f)$ of α are respectively defined in the following manner.

$$\delta(\alpha; f) = 1 - \limsup_{r\to\infty} \frac{N(r,\alpha; f)}{T(r, f)} = \liminf_{r\to\infty} \frac{m(r,\alpha; f)}{T(r, f)}$$

and

$$\Delta(\alpha; f) = 1 - \liminf_{r\to\infty} \frac{N(r,\alpha; f)}{T(r, f)} = \limsup_{r\to\infty} \frac{m(r,\alpha; f)}{T(r, f)}$$

Milloux[1] introduced the concept of absolute defect of α with respect to the derivative f. Later Xiong[2] extended this definition. He introduced the term

$$\delta_R^{(k)}(\alpha; f) = 1 - \limsup_{r\to\infty} \frac{N(r, \alpha; f^{(k)})}{T(r, f)}$$

for $k = 1,2,3....$ and called it the relative Nevalinna defect of α with respect to $f(k)$. Xiong[2] has shown various relations between the usual defects and the relative defects. Singh[3] introduced the term relative defect for distinct zeros and poles and established various relations between it, relative defects and the usual defects.

In the paper we call the term

$$\Delta_R^{(k)}(\alpha; f) = 1 - \liminf_{r\to\infty} \frac{N(r, \alpha; f^{(k)})}{T(r, f)}$$

the relative Valiron defect of α with respect to $f^{(k)}$ for $k = 1,2,3,...$ and prove various relations between it and the relative Nevanlinna defect.

The term $S(r, f)$ denotes any quantity satisfying $S(r, f) = o\{T(r, f)\}$ as $r \to \infty$ through all values of r if f is of finite order and except possibly for a set of r of finite linear measure otherwise. We do not explain the standard definitions and notations of the value distribution theory and the Nevanlinna theory as those are available in Hayman[4].

Lemmas

In this section we present the lemmas which will be needed in the sequel.

Lemma 1 [Singh[5]] : Let f be a meromorphic

function of finite order such that $\sum_{a\neq\infty}\delta(a;f)=1$ and $\delta(\infty;f)=1$. Then for any non-negative integer k,

$$\lim_{r\to\infty}\frac{T(r,f^{(k)})}{T(r,f)}=1.$$

Lemma 2 [Singh 5] : Let f be a meromorphic function of finite order with $\sum_{a\neq\infty}\delta(a;f)=\delta(\infty;f)=1$. Then for any $\alpha, \delta_R^{(k)}(\alpha;f)=\liminf_{r\to\infty}\frac{m(r,\alpha;f^{(k)})}{T(r,f)}$.

Lemma 3 : Let f be a meromorphic function of finite order such that $\sum_{a\neq\infty}\delta(a;f)=\delta(\infty;f)=1$. Then for any $\Delta_R^{(k)}(\alpha;f)=\limsup_{r\to\infty}\frac{m(r,\alpha;f^{(k)})}{T(r,f)}$. The proof is omitted.

Theorems

In this section we present the main results of the paper.

Theorem 1 : Let f be a meromorphic function of finite order. Then for any positive integer k, $\Delta(\infty,f)+\Delta_R^{(k)}(0,f)\geq\delta(0,f)+\delta(a,f)+\Delta_R^{(k)}(\infty,f)$, where a is any non zero finite complex number.

Proof : Let us consider the following identity.

$$\frac{a}{f}=1-\frac{f-a}{f^{(k)}}.\frac{f^{(k)}}{f}$$

Since $m\left(r,\frac{1}{f}\right)\leq m\left(r,\frac{a}{f}\right)+O(1)$, we get from the above identity

$$m\left(r,\frac{1}{f}\right)\leq m\left(r,\frac{f-a}{f^{(k)}}\right)+S(r,f). \qquad (1)$$

Now by Nevanlinna's first fundamental theorem and Milloux's theorem {p. 55, Hayman[4]} it follows from (1)

$$m\left(r,\frac{1}{f}\right)\leq T\left(r,\frac{f-a}{f^{(k)}}\right)-N\left(r,\frac{f-a}{f^{(k)}}\right)+S(r,f)$$

i.e., $$m\left(r,\frac{1}{f}\right)\leq T\left(r,\frac{f^{(k)}}{f-a}\right)-N\left(r,\frac{f-a}{f^{(k)}}\right)+S(r,f)$$

i.e., $$m\left(r,\frac{1}{f}\right)\leq N\left(r,\frac{f^{(k)}}{f-a}\right)-N\left(r,\frac{f-a}{f^{(k)}}\right)+S(r,f) \qquad (2)$$

In view of {p. 34, Hayman[4]} it follows from (2)

$$m\left(r,\frac{1}{f}\right)\leq N(r,f^{(k)})+N\left(r,\frac{1}{f-a}\right)$$

$$-N(r,f-a)-N\left(r,\frac{1}{f^{(k)}}\right)+S(r,f)$$

i.e. $$\liminf_{r\to\infty}\frac{m\left(r,\frac{1}{f}\right)}{T(r,f)}$$

$$\leq\liminf_{r\to\infty}\left\{\frac{N(r,f^{(k)})}{T(r,f)}-\frac{N(r,f)}{T(r,f)}-\frac{N\left(r,\frac{1}{f^{(k)}}\right)}{T(r,f)}\right\}$$

$$+\limsup_{r\to\infty}\frac{N\left(r,\frac{1}{f-a}\right)}{T(r,f)}$$

$$\leq\liminf_{r\to\infty}\frac{N(r,f^{(k)})}{T(r,f)}-\liminf_{r\to\infty}\frac{N(r,f)}{T(r,f)}$$

$$-\liminf_{r\to\infty}\frac{N\left(r,\frac{1}{f^{(k)}}\right)}{T(r,f)}+\limsup_{r\to\infty}\frac{N\left(r,\frac{1}{f-a}\right)}{T(r,f)}$$

i.e., $\delta(0,f)\le\left\{1-\Delta_R{}^{(k)}(\infty,f)\right\}-\{1-\Delta(\infty,f)\}$

$$-\left\{1-\Delta_R{}^{(k)}(0,f)\right\}+\{1-\delta(a,f)\}$$

i.e., $\Delta(\infty,f)+\Delta_R{}^{(k)}(0,f)\ \ge\ \delta(0,f)+\delta(a,f)$

$$+\Delta_R{}^{(k)}(\infty,f).$$

This proves the theorem.

Remark 1 : The sign $\ge$ in Theorem 1 cannot be replaced by $>$ only. This is evident from the following example.

Example 1 : Let f = exp z.

Then $\Delta(\infty,f)=\Delta_R{}^{(k)}(0,f)=\Delta_R{}^{(k)}(\infty,f)=1$ and $\delta(0,f)=\delta(\infty,f)=1.$

So $\delta(a,f)=0.$

Then $\Delta(\infty,f)+\Delta_R{}^{(k)}(0,f)=2=\delta(a,f)$

$$+\Delta_R{}^{(k)}(\infty,f).$$

Theorem 2 : Let f be a meromorphic function of finite order such that $\sum_{a\neq\infty}\delta(a;f)=\delta(\infty;f)=1.$ Then for any positive integer k,

$$\Delta_R{}^{(k)}(0,f)\ \ge\ \delta(0,f).$$

Proof : Since $f=f^{(k)}\cdot\frac{f}{f^{(k)}}$ we get,

$$m\,(r,f)\le m\left(r,f^{(k)}\right)+m\left(r,\frac{f}{f^{(k)}}\right)\qquad(3)$$

Now by Nevanlinna's first fundamental theorem and Milloux's theorem {p. 55, Hayman[4]} we obtain from (3)

$$m(r,f)\le m\left(r,f^{(k)}\right)+T\left(r,\frac{f}{f^{(k)}}\right)-N\left(r,\frac{f}{f^{(k)}}\right)$$

i.e., $m(r,f)\le m\left(r,f^{(k)}\right)+T\left(r,\frac{f^{(k)}}{f}\right)$

$$-N\left(r,\frac{f}{f^{(k)}}\right)+O(1)$$

i.e., $m(r,f)\le m\left(r,f^{(k)}\right)+N\left(r,\frac{f^{(k)}}{f}\right)$

$$-N\left(r,\frac{f}{f^{(k)}}\right)+S(r,f)\qquad(4)$$

Now in view of {p. 34, Hayman[4]} it follows from (4)

$$m(r,f)\le m\left(r,f^{(k)}\right)+N\left(r,f^{(k)}\right)+N\left(r,\frac{1}{f}\right)$$

$$-N(r,f)-N\left(r,\frac{f}{f^{(k)}}\right)+S(r,f)$$

i.e., $\liminf_{r\to\infty}\frac{m(r,f)}{T(r,f)}\le\liminf_{r\to\infty}\left\{\frac{N\left(r,f^{(k)}\right)}{T(r,f)}\right.$

$$\left.-\frac{N(r,f)}{T(r,f)}-\frac{N\left(r,\frac{1}{f^{(k)}}\right)}{T(r,f)}\right\}$$

$$+\limsup_{r\to\infty}\left\{\frac{N\left(r,\frac{1}{f}\right)}{T(r,f)}+\frac{m\left(r,f^{(k)}\right)}{T(r,f)}\right\}$$

$$\leq \liminf_{r\to\infty}\frac{N\left(r,f^{(k)}\right)}{T(r,f)}-\liminf_{r\to\infty}\frac{N(r,f)}{T(r,f)}$$

$$-\liminf_{r\to\infty}\frac{N\left(r,\frac{1}{f^{(k)}}\right)}{T(r,f)}+\limsup_{r\to\infty}\frac{N\left(r,\frac{1}{f}\right)}{T(r,f)}$$

$$+\limsup_{r\to\infty}\frac{m\left(r,f^{(k)}\right)}{T(r,f)} \qquad (5)$$

Since $\delta(\infty,f)=\Delta(\infty,f)=1$, by Lemma 3 we obtain from (5)

$$\delta(\infty,f)\leq\left\{1-\Delta_R{}^{(k)}(\infty,f)\right\}-\left\{1-\Delta(\infty,f)\right\}$$

$$-\left\{1-\Delta_R{}^{(k)}(0,f)\right\}+\left\{1-\delta(0,f)\right\}+\Delta_R{}^{(k)}(\infty,f)$$

i.e., $\Delta_R{}^{(k)}(0,f)\geq\delta(0,f)$.

Thus the theorem is established.

Remark 2 : Considering f = exp z one can easily verify that $\geq$ cannot be replaced by $>$ only in Theorem 2.

Theorem 3 : Let f be a meromorphic function of finite order and a, b be any two distinct finite complex numbers. Then for any positive integer k,

$$\Delta_R{}^{(k)}(0,f)+\Delta(\infty,f)\geq\Delta_R{}^{(k)}(\infty,f)+\delta(a,f)$$

$$+1/2\,\delta(b,f).$$

Proof : Considering the identity

$$\frac{b-a}{f-a}=\frac{f^{(k)}}{f-a}\left\{\frac{f-a}{f^{(k)}}-\frac{f-b}{f^{(k)}}\right\}$$

we obtain in view of Milloux's theorem {p. 55, Hayman[4]}

$$m\left(r,\frac{b-a}{f-a}\right)\leq m\left(r,\frac{f-a}{f^{(k)}}\right)+m\left(r,\frac{f-b}{f^{(k)}}\right)+S(r,f)$$

i.e. $$m\left(r,\frac{b-a}{f-a}\right)\leq T\left(r,\frac{f-a}{f^{(k)}}\right)-N\left(r,\frac{f-a}{f^{(k)}}\right)$$

$$+T\left(r,\frac{f-b}{f^{(k)}}\right)-N\left(r,\frac{f-b}{f^{(k)}}\right)+S(r,f). \qquad (6)$$

Since $m\left(r,\frac{1}{f-a}\right)\leq m\left(r,\frac{b-a}{f-a}\right)+O(1)$

and $T(r,f)=T\left(r,\frac{1}{f}\right)+O(1)$,

it follows from (6)

$$m\left(r,\frac{1}{f-a}\right)\leq N\left(r,\frac{f^{(k)}}{f-a}\right)-N\left(r,\frac{f-a}{f^{(k)}}\right)$$

$$+N\left(r,\frac{f^{(k)}}{f-b}\right)-N\left(r,\frac{f-b}{f^{(k)}}\right)+S(r,f). \qquad (7)$$

In view of {p. 34, Hayman[4]} we get from (7)

$$m\left(r,\frac{1}{f-a}\right)\leq N\left(r,f^{(k)}\right)+N\left(r,\frac{1}{f-a}\right)$$

$$-N(r,f-a)-N\left(r,\frac{1}{f^{(k)}}\right)$$

$$+N\left(r,f^{(k)}\right)+N\left(r,\frac{1}{f-b}\right)-N(r,f-b)$$

$$-N\left(r,\frac{1}{f^{(k)}}\right)+S(r,f)$$

i.e.,

$$\liminf_{r\to\infty}\frac{m\left(r,\frac{1}{f-a}\right)}{T(r,f)}\le 2\liminf_{r\to\infty}\left\{\frac{N\left(r,f^{(k)}\right)}{T(r,f)}-\frac{N\left(r,\frac{1}{f^{(k)}}\right)}{T(r,f)}-\frac{N(r,f)}{T(r,f)}\right\}$$

$$+\limsup_{r\to\infty}\left\{\frac{N\left(r,\frac{1}{f-a}\right)}{T(r,f)}+\frac{N\left(r,\frac{1}{f-b}\right)}{T(r,f)}\right\}$$

$$\le 2\left\{\liminf_{r\to\infty}\frac{N\left(r,f^{(k)}\right)}{T(r,f)}-\liminf_{r\to\infty}\frac{N\left(r,\frac{1}{f^{(k)}}\right)}{T(r,f)}-\liminf_{r\to\infty}\frac{N(r,f)}{T(r,f)}\right\}$$

$$+\limsup_{r\to\infty}\frac{N\left(r,\frac{1}{f-a}\right)}{T(r,f)}+\limsup_{r\to\infty}\frac{N\left(r,\frac{1}{f-b}\right)}{T(r,f)}$$

i.e.,

$$\delta(a,f)\le 2\left\{1-\Delta_R^{(k)}(\infty,f)\right\}-2\left\{1-\Delta_R^{(k)}(0,f)\right\}$$

$$-2\left\{1-\Delta(\infty,f)\right\}+\left\{1-\delta(a,f)\right\}+\left\{1-\delta(b,f)\right\}$$

i.e.,

$$2\delta(a,f)\le 2\Delta_R^{(k)}(0,f)+2\Delta(\infty,f)$$

$$-2\Delta_R^{(k)}(\infty,f)-\delta(b,f)$$

i.e.,

$$\Delta_R^{(k)}(0,f)+\Delta(\infty,f)\ge\Delta_R^{(k)}(\infty,f)$$

$$+\delta(a,f)+\tfrac{1}{2}\,\delta(b,f).$$

This proves the theorem.

Theorem 4 : Let f be any meromorphic function of finite order and n be any positive integer. Then for every integer $k\,(0\le k<n)$

$$\Delta_R^{(k)}(\infty,f)+\Delta_R^{(n)}(0,f)\ge\Delta_R^{(n)}(\infty,f)$$

$$+\delta_R^{(k)}(a,f)+\delta(a,f),$$

where a is any finite non zero complex number.

Proof : From the identity

$$\frac{1}{f-a}=\frac{1}{a}\left(\frac{f^{(k)}}{f-a}-\frac{f^{(k)}-a}{f^{(n)}}\frac{f^{(n)}}{f-a}\right)$$

and by Milloux's theorem {p 55, Hayman[4]} we get,

$$m\left(r,\frac{1}{f-a}\right)\le m\left(r,\frac{f^{(k)}-a}{f^{(n)}}\right)+S(r,f). \tag{8}$$

Now by Nevanlinna's first fundamental theorem it follows from (8)

$$m\left(r,\frac{1}{f-a}\right)\le T\left(r,\frac{f^{(k)}-a}{f^{(n)}}\right)-N\left(r,\frac{f^{(k)}-a}{f^{(n)}}\right)+S(r,f)$$

$$=T\left(r,\frac{f^{(n)}}{f^{(k)}-a}\right)-N\left(r,\frac{f^{(k)}-a}{f^{(n)}}\right)+S(r,f)$$

$$=N\left(r,\frac{f^{(n)}}{f^{(k)}-a}\right)-N\left(r,\frac{f^{(k)}-a}{f^{(n)}}\right)+S(r,f). \tag{9}$$

Now in view of {p. 34, Hayman[4]} we obtain from (9)

$$m\left(r, \frac{1}{f-a}\right) \leq N\left(r, f^{(n)}\right) + N\left(r, \frac{1}{f^{(k)}-a}\right)$$

$$- N\left(r, f^{(k)} - a\right) - N\left(r, \frac{1}{f^{(n)}}\right) + S(r, f)$$

i.e., $$\liminf_{r\to\infty} \frac{m\left(r, \frac{1}{f-a}\right)}{T(r,f)} \leq \liminf_{r\to\infty} \left\{ \frac{N\left(r, f^{(n)}\right)}{T(r,f)} - \frac{N\left(r, f^{(k)}\right)}{T(r,f)} - \frac{N\left(r, \frac{1}{f^{(n)}}\right)}{T(r,f)} \right\}$$

$$+ \limsup_{r\to\infty} \left\{ \frac{N\left(r, \frac{1}{f^{(k)}-a}\right)}{T(r,f)} \right\}$$

i.e. $$\liminf_{r\to\infty} \frac{m\left(r, \frac{1}{f-a}\right)}{T(r,f)}$$

$$\leq \liminf_{r\to\infty} \frac{N\left(r, f^{(n)}\right)}{T(r,f)} - \liminf_{r\to\infty} \frac{N\left(r, f^{(k)}\right)}{T(r,f)}$$

$$- \liminf_{r\to\infty} \frac{N\left(r, \frac{1}{f^{(n)}}\right)}{T(r,f)} + \limsup_{r\to\infty} \frac{N\left(r, \frac{1}{f^{(k)}-a}\right)}{T(r,f)}$$

i.e. $$\delta(a,f) \leq \left\{1 - \Delta_R{}^{(n)}(\infty, f)\right\} - \left\{1 - \Delta_R{}^{(k)}(\infty, f)\right\}$$

$$- \left\{1 - \Delta_R{}^{(n)}(0, f)\right\} + \left\{1 - \delta_R{}^{(k)}(a, f)\right\}$$

i.e. $$\Delta_R{}^{(k)}(\infty, f) + \Delta_R{}^{(n)}(0, f) \geq \Delta_R{}^{(n)}(\infty, f)$$

$$+ \delta_R{}^{(k)}(a, f) + \delta(a, f)$$

This proves the theorem.

Theorem 5 : Let f be a meromorphic function of finite order such that $\sum_{\alpha\neq\infty} \delta(\alpha; f) = \delta(\infty; f) = 1$, a be a finite complex number and b, c be two distinct nonzero complex numbers. Then for any positive integer k

$$\Delta(a; f) + \delta_R{}^{(k)}(b; f) + \delta_R{}^{(k)}(c; f) \leq 2.$$

Proof : Since $\frac{1}{f-a} = \frac{f^{(k)}}{f-a} \cdot \frac{1}{f^{(k)}}$ by Milloux's theorem {p. 55, Hayman[4]} we obtain

$$m\left(r, \frac{1}{f-a}\right) \leq m\left(r, \frac{1}{f^{(k)}}\right) + S(r, f). \tag{10}$$

Applying Nevanlinna's first fundamental theorem we get from (10)

$$m\left(r, \frac{1}{f-a}\right) \leq T\left(r, f^{(k)}\right) - N\left(r, \frac{1}{f^{(k)}}\right) + S(r, f). \tag{11}$$

Now by Nevanlinna's second fundamental theorem and Lemma 1 it follows from (11)

$$m\left(r, \frac{1}{f-a}\right) \leq \overline{N}\left(r, \frac{1}{f^{(k)}}\right) + \overline{N}\left(r, \frac{1}{f^{(k)}-b}\right)$$

$$+ \overline{N}\left(r, \frac{1}{f^{(k)}-c}\right) - N\left(r, \frac{1}{f^{(k)}}\right) + S(r, f). \tag{12}$$

Since $+\overline{N}\left(r, \frac{1}{f^{(k)}}\right) - N\left(r, \frac{1}{f^{(k)}}\right) \leq 0$, we obtain from (12)

$$m\left(r, \frac{1}{f-a}\right) \leq N\left(r, \frac{1}{f^{(k)}-b}\right)$$

$$+N\left(r,\ \frac{1}{f^{(k)}-c}\right)+S(r,f)$$

i.e.,

$$m\left(r,\ \frac{1}{f-a}\right)\le T\left(r,\ \frac{1}{f^{(k)}-b}\right)-m\left(r,\ \frac{1}{f^{(k)}-b}\right)$$

$$+T\left(r,\ \frac{1}{f^{(k)}-c}\right)-m\left(r,\ \frac{1}{f^{(k)}-c}\right)+S(r,f)$$

i.e., $$m\left(r,\ \frac{1}{f-a}\right)\le 2T\left(r,f^{(k)}\right)-m\left(r,\ \frac{1}{f^{(k)}-b}\right)$$

$$-m\left(r,\ \frac{1}{f^{(k)}-c}\right)+S(r,f)$$

i.e., $$\limsup_{r\to\infty}\frac{m\left(r,\ \frac{1}{f-a}\right)}{T(r,f)}\le 2\limsup_{r\to\infty}\frac{T\left(r,f^{(k)}\right)}{T(r,f)}$$

$$-\liminf_{r\to\infty}\frac{m\left(r,\ \frac{1}{f^{(k)}-b}\right)}{T(r,f)}-\liminf_{r\to\infty}\frac{m\left(r,\ \frac{1}{f^{(k)}-c}\right)}{T(r,f)} \tag{13}$$

Now by Lemma 1 and Lemma 2 we get from (13)

$$\Delta(a,f)\le 2-\delta_R^{(k)}(b,f)-\delta_R^{(k)}(c,f)$$

i.e., $$\Delta(a,f)+\delta_R^{(k)}(b,f)+\delta_R^{(k)}(c,f)\le 2.$$

This proves the theorem.

Theorem 6 : Let f be a meromorphic function of finite order satisfying $\sum\limits_{a\ne\infty}\delta(a;f)=1$ and $\delta(\infty;f)=1$. Then for any positive integer k,

$\delta(0,f)+\delta_R^{(k)}(\alpha,f)\le 1$ where α is a non zero finite complex number.

Proof : Considering the identity

$$\frac{\alpha}{f}=\frac{f^{(k)}}{f}-\frac{f^{(k)}-\alpha}{f^{(k+1)}}\cdot\frac{f^{(k+1)}}{f}$$

we get in view of Milloux's theorem {p. 55, Hayman[4]} and Nevanlinna's first fundamental theorem,

$$m\left(r,\ \frac{1}{f}\right)\le m\left(r,\ \frac{f^{(k)}-\alpha}{f^{(k+1)}}\right)+S(r,f)$$

i.e., $$m\left(r,\frac{1}{f}\right)\le T\left(r,\frac{f^{(k)}-\alpha}{f^{(k+1)}}\right)-N\left(r,\frac{f^{(k)}-\alpha}{f^{(k+1)}}\right)+S(r,f)$$

i.e., $$m\left(r,\frac{1}{f}\right)\le T\left(r,\frac{f^{(k+1)}}{f^{(k)}-\alpha}\right)-N\left(r,\frac{f^{(k)}-\alpha}{f^{(k+1)}}\right)+S(r,f)$$

i.e., $$m\left(r,\frac{1}{f}\right)\le N\left(r,\frac{f^{(k+1)}}{f^{(k)}-\alpha}\right)-N\left(r,\frac{f^{(k)}-\alpha}{f^{(k+1)}}\right)+S(r,f). \tag{14}$$

Now in view of {p. 34, Hayman[4]} it follows from (14),

$$m\left(r,\ \frac{1}{f}\right)\le N\left(r,f^{(k+1)}\right)+N\left(r,\ \frac{1}{f^{(k)}-\alpha}\right)$$

$$-N\left(r,f^{(k)}-\alpha\right)-N\left(r,\ \frac{1}{f^{(k+1)}}\right)+S(r,f)$$

i.e., $$m\left(r,\ \frac{1}{f}\right)\le\left\{N\left(r,\ \frac{1}{f^{(k)}-\alpha}\right)-N\left(r,\ \frac{1}{f^{(k+1)}}\right)\right\}$$

$$+\left\{N\left(r,f^{(k+1)}\right)-N\left(r,f^{(k)}\right)\right\}+S(r,f)$$

i.e., $$m\left(r,\ \frac{1}{f}\right)\le N\left(r,\ \alpha;f^{(k)}\right)+\overline{N}(r,f)+S(r,f).$$

Since $\delta(\infty,f)=1$, it follows that $\lim\limits_{r\to\infty}\frac{\overline{N}(r,f)}{T(r,f)}=0.$

So from above we get

$$\liminf_{r\to\infty} \frac{m(r, 0; f)}{T(r, f)} \le \liminf_{r\to\infty} \frac{N\left(r, \alpha; f^{(k)}\right)}{T(r, f)}$$

i.e., $\delta(0, f) + \Delta_R^{(k)}(\alpha, f) \le 1.$

Since $\sum_{a\ne\infty} \delta(a; f) = \delta(\infty; f) = 1$, by Lemma 3 we note that $\Delta_R^{(k)}(\alpha; f) \ge 0$. This proves the theorem.

Remark 3 : The inequality in Theorem 6 is best possible in the sense that $\le$ cannot be replaced by $<$ which is evident from the following example.

Example 3 : Let $f = \exp z$.

So $\delta(0, f) = 1$ and $\delta_R^{(k)}(0, f) = \delta_R^{(k)}(\infty, f) = 1.$

Now by Nevanlinna's second fundamental theorem and in view of above we get

$$T\left(r, f^{(k)}\right) \le N\left(r, a; f^{(k)}\right) + S\left(r, f^{(k)}\right)$$

$$\le T\left(r, f^{(k)}\right) + S\left(r, f^{(k)}\right)$$

i.e., $$\frac{T\left(r, f^{(k)}\right)}{T(r, f)} \le \frac{N\left(r, a; f^{(k)}\right)}{T(r, f)} + \frac{S\left(r, f^{(k)}\right)}{T\left(r, f^{(k)}\right)} \cdot \frac{T\left(r, f^{(k)}\right)}{T(r, f)}$$

$$\le \frac{T\left(r, f^{(k)}\right)}{T(r, f)} + \frac{S\left(r, f^{(k)}\right)}{T\left(r, f^{k}\right)} \cdot \frac{T\left(r, f^{(k)}\right)}{T(r, f)}.$$

By Lemma 1 it follows from above that,

$$\lim_{r\to\infty} \frac{N\left(r, a; f^{(k)}\right)}{T(r, f)} = 1.$$

Therefore $\Delta_R^{(k)}(\alpha, f) = 0.$

Thus $\delta(0, f) + \Delta_R^{(k)}(\alpha, f) = 1$

Theorem 7 : Let k be any positive integer and a be a finite complex number. Then for any meromorphic function f of finite order satisfying

$$\sum_{\alpha\ne\infty} \delta(\alpha; f) = \delta(\infty; f) = 1.$$

$$\Delta_R^{(k)}(a, f) \ge \delta_R^{(k)}(a, f) + \delta(0, f).$$

Proof : Let $b \ne a$ be a finite complex number.

Since $$\frac{a-b}{f^{(k)}-a} = \frac{f}{f^{(k)}-a}\left\{\frac{f^{(k)}-b}{f} - \frac{f^{(k)}-a}{f}\right\}$$

we obtain in view of Milloux's theorem {p. 55, Hayman[4]} and Nevanlinna's first fundamental theorem,

$$m\left(r, \frac{a-b}{f^{(k)}-a}\right) \le m\left(r, \frac{f}{f^{(k)}-a}\right) + S(r, f)$$

i.e., $$m\left(r, \frac{1}{f^{(k)}-a}\right) \le T\left(r, \frac{f}{f^{(k)}-a}\right) - N\left(r, \frac{f}{f^{(k)}-a}\right) + S(r, f)$$

i.e., $$m\left(r, \frac{1}{f^{(k)}-a}\right) \le T\left(r, \frac{f^{(k)}-a}{f}\right) - N\left(r, \frac{f}{f^{(k)}-a}\right) + S(r, f)$$

i.e., $$m\left(r, \frac{1}{f^{(k)}-a}\right) \le N\left(r, \frac{f^{(k)}-a}{f}\right)$$

$$-N\left(r, \frac{f}{f^{(k)}-a}\right) + S(r,f) \qquad (15)$$

In view of {p. 34, Hayman[4]} it follows from (15)

$$m\left(r, \frac{1}{f^{(k)}-a}\right) \le N\left(r, f^{(k)}-a\right) + N\left(r, \frac{1}{f}\right)$$

$$-N(r,f) - N\left(r, \frac{1}{f^{(k)}-a}\right) + S(r,f)$$

i.e., $$\liminf_{r\to\infty} \frac{m\left(r, \frac{1}{f^{(k)}-a}\right)}{T(r,f)}$$

$$\le \liminf_{r\to\infty}\left\{\frac{N\left(r,f^{(k)}\right)}{T(r,f)} - \frac{N(r,f)}{T(r,f)} - \frac{N\left(r, \frac{1}{f^{(k)}-a}\right)}{T(r,f)}\right\}$$

$$+ \limsup_{r\to\infty} \frac{N\left(r, \frac{1}{f}\right)}{T(r,f)}$$

i.e., $$+ \liminf_{r\to\infty} \frac{m\left(r, \frac{1}{f^{(k)}-a}\right)}{T(r,f)}$$

$$\le \liminf_{r\to\infty} \frac{N\left(r,f^{(k)}\right)}{T(r,f)} - \liminf_{r\to\infty} \frac{N(r,f)}{T(r,f)}$$

$$- \liminf_{r\to\infty} \frac{N\left(r, \frac{1}{f^{(k)}-a}\right)}{T(r,f)} + \limsup_{r\to\infty} \frac{N\left(r, \frac{1}{f}\right)}{T(r,f)} \qquad (16)$$

Since $\delta(\infty, f) = 1, \ \lim_{r\to\infty} \frac{N(r,f)}{T(r,f)} = \lim_{r\to\infty} \frac{\overline{N}(r,f)}{T(r,f)} = 0$

and so $$\lim_{r\to\infty} \frac{N\left(r,f^{(k)}\right)}{T(r,f)} = \lim_{r\to\infty} \frac{N(r,f)}{T(r,f)}$$

$$+k \lim_{r\to\infty} + \frac{\overline{N}(r,f)}{T(r,f)} = 0$$

Thus by Lemma 2 it follows from (16)

$$\delta_R^{(k)}(a,f) \le \Delta_R^{(k)}(a,f) - 1 + \{1-\delta(0,f)\}$$

i.e., $$\Delta_R^{(k)}(a,f) \ge \delta_R^{(k)}(a,f) + \delta(0,f).$$

This proves the theorem.

Theorem 8 : Let f be a meromorphic function of finite order such that $\sum_{\alpha\neq\infty} \delta(\alpha; f) = \delta(\alpha; f) = 1$ and $a_1, a_2, \ldots a_q$ are all distinct finite complex numbers. Also let n be a positive integer. Then for any positive integer $k>n$.

$$\sum_{i=1}^{q} \Delta_R^{(k)}(a_i; f) + \Delta_R^{(n)}(0,f)$$

$$\ge \sum_{i=1}^{q} \delta_R^{(k)}(a_i; f) + q\,\delta_R^{(n)}(0,f)$$

Proof : Let $F = \sum_{i=1}^{q} \frac{1}{f^{(k)}-a_i}$ for $i = 1,2, \ldots q$

Then we get {cf. p. 33, Hayman[4]}

$$\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right) \le m(r,F) + O(1)$$

i.e., $$\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right) \le m\left(r, \sum_{i=1}^{q} \frac{f^{(n)}}{f^{(k)}-a_i}\right)$$

$$+ m\left(r, \frac{1}{f^{(n)}}\right) + O(1)$$

i.e., $$\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right) \leq \sum_{i=1}^{q} m\left(r, \frac{f^{(n)}}{f^{(k)}-a_i}\right) + m\left(r, \frac{1}{f^{(n)}}\right) + O(1)$$

i.e., $$\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right) \leq \sum_{i=1}^{q} \left\{T\left(r, \frac{f^{(n)}}{f^{(k)}-a_i}\right) - N\left(r, \frac{f^{(n)}}{f^{(k)}-a_i}\right)\right\} + m\left(r, \frac{1}{f^{(n)}}\right) + O(1)$$

i.e., $$\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right) \leq \sum_{i=1}^{q} \left\{T\left(r, \frac{f^{(k)}-a_i}{f^{(n)}}\right) - N\left(r, \frac{f^{(n)}}{f^{(k)}-a_i}\right)\right\} + m\left(r, \frac{1}{f^{(n)}}\right) + O(1)$$

i.e., $$\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right) \leq \sum_{i=1}^{q} \left\{N\left(r, \frac{f^{(k)}-a_i}{f^{(n)}}\right) - N\left(r, \frac{f^{(n)}}{f^{(k)}-a_i}\right)\right\} + m\left(r, \frac{1}{f^{(n)}}\right) + S(r, f) \quad (17)$$

In view of {p. 34, Hayman[4]} we get from (17)

$$\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right) \leq m\left(r, \frac{1}{f^{(n)}}\right) + \sum_{i=1}^{q} \left\{N\left(r, f^{(k)}-a_i\right) + N\left(r, \frac{1}{f^{(n)}}\right) - N\left(r, f^{(n)}\right) - N\left(r, \frac{1}{f^{(k)}-a_i}\right)\right\} + S(r, f)$$

$$= m\left(r, \frac{1}{f^{(n)}}\right) + q\,N\left(r, f^{(k)}\right) + q\,N\left(r, \frac{1}{f^{(n)}}\right) - q\,N\left(r, f^{(n)}\right) - \sum_{i=1}^{q} N\left(r, \frac{1}{f^{(k)}-a_i}\right) + S(r, f).$$

i.e., $$\liminf_{r\to\infty} \frac{\sum_{i=1}^{q} m\left(r, \frac{1}{f^{(k)}-a_i}\right)}{T(r, f)}$$

$$\leq \liminf_{r\to\infty} \left\{\frac{qN\left(r, f^{(k)}\right)}{T(r, f)} - \frac{qN\left(r, f^{(k)}\right)}{T(r, f)} - \frac{\sum_{i=1}^{q} N\left(r, \frac{1}{f^{(k)}-a_i}\right)}{T(r, f)}\right\} +$$

$$\limsup_{r\to\infty} \left\{\frac{m\left(r, \frac{1}{f^{(n)}}\right)}{T(r, f)} + \frac{qN\left(r, \frac{1}{f^{(n)}}\right)}{T(r, f)}\right\}$$

i.e., $$\sum_{i=1}^{q} \liminf_{r\to\infty} \frac{m\left(r, \frac{1}{f^{(k)}-a_i}\right)}{T(r, f)}$$

$$\leq q \liminf_{r\to\infty} \frac{N\left(r, f^{(k)}\right)}{T(r, f)} - q \liminf_{r\to\infty} \frac{N\left(r, f^{(n)}\right)}{T(r, f)}$$

$$\sum_{i=1}^{q} \liminf_{r\to\infty} \frac{N\left(r, \frac{1}{f^{(k)}-a_i}\right)}{T(r, f)} + \limsup_{r\to\infty} \frac{m\left(r, \frac{1}{f^{(n)}}\right)}{T(r, f)}$$

$$+ q \limsup_{r\to\infty} \frac{N\left(r, \frac{1}{f^{(n)}}\right)}{T(r,f)}. \qquad (18)$$

Since $\delta(\infty, f) = 1$, $\lim\limits_{r\to\infty} \frac{N(r,f)}{T(r,f)} = \lim\limits_{r\to\infty} \frac{\overline{N}(r,f)}{T(r,f)} = 0$.

So $\lim\limits_{r\to\infty} \frac{N\left(r, f^{(k)}\right)}{T(r,f)} = \lim\limits_{r\to\infty} \frac{N(r,f)}{T(r,f)} + k \lim\limits_{r\to\infty} \frac{\overline{N}(r,f)}{T(r,f)} = 0$.

Similarly, $\lim\limits_{r\to\infty} \frac{N\left(r, f^{(n)}\right)}{T(r,f)} = 0.$

Now by Lemma 2 and Lemma 3 it follows from (18),

$$\sum_{i=1}^{q} \delta_R^{(k)}(a_i, f) \le \sum_{i=1}^{q} \Delta_R^{(k)}(a_i, f) - q + \Delta_R^{(n)}(0, f) + q\left\{1 - \delta_R^{(n)}(0, f)\right\}$$

i.e., $\sum\limits_{i=1}^{q} \Delta_R^{(k)}(a_i, f) + \Delta_R^{(n)}(0, f)$

$$\ge \sum_{i=1}^{q} \delta_R^{(k)}(a_i, f) + q\,\delta_R^{(n)}(0, f).$$

This proves the theorem.

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On dispersion relation of electro-magneto-visco-elastic plane waves

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Abstract

A study is made of propagation of electro-magneto-visco-elastic plane waves in an electrically conducting infinite elastic solid permeated by a primary uniform magnetic field. A more general dispersion relation is deduced showing the effects of applied magnetic field and visco elastic parameters on the phase velocity of the waves. It is seen that if the primary magnetic field has both longitudinal and transverse components the displacement components u, v and the perturbed magnetic field b_2 are linked together. The coupled magneto-visco-elastic plane waves characterized by the dispersion equation are damped and dispersive.

(**Keywords** : electro-magneto-visco-elastic plane waves/ dispersion relation/elastic solid)

Introduction

The propagation of elastic waves in a non-rotating electrically conducting medium under the action of an external magnetic field was first investigated by Knopoff[1] and later by several authors[2-5]. Parkus[4,5] considered recent developments of magneto-elastic and magneto-thermo elasticity in non-rotating elastic media. It may be mentioned that Roy Choudhuri and Debnath[6] have studied propagation of plane waves in an infinite elastic medium permeated by an external magnetic field. Ersoy[7] studied plane waves in an electrically conducting and magnetizable visco-elastic isotropic solids of Kelvin-Voigt type. On the consideration of visco-elastic nature of the earth [Peltier[8]], it seems relevant to study propagation of magneto-visco-elastic plane waves in an electrically conducting visco-elastic medium under the action of an external magnetic field.

The main aim of the present study is to investigate the time harmonic progressive plane waves in an electrically conducting infinite visco-elastic solid of Kelvin-Voigt type permeated by a primary uniform magnetic field. Special attention has been paid to the interaction between electro-magnetic field and visco-elastic field and effect of visco-elastic parameters and the external magnetic field on the propagation of coupled waves. It is seen that if the primary magnetic field has both longitudinal and transverse components the displacement components u, v and the perturbed magnetic field b_2 are linked together. The coupled magneto-visco-elastic plane waves characterized by the dispersion equation are damped and dispersive.

Formulation of the Problem and the Basic Equations

We consider an infinite, isotropic, electrically conducting, elastic solid permeated by a primary magnetic field $\mathbf{B}_0 = (B_1, B_2, B_3)$. The elastic solid is characterized by the density ρ, Lame constants λ, μ.

The displacement equation of motion in magneto-visco-elasticity is

$$\rho\ddot{\mathbf{u}} = (\lambda+\mu)\nabla(\nabla.\mathbf{u}) + (\lambda'+\mu^{1})\frac{\partial}{\partial t}\nabla(\nabla.\mathbf{u}) +$$

$$\mu\nabla^2\mathbf{u} + \mu'\frac{\partial}{\partial t}\nabla^2\mathbf{u} + \mathbf{J}\times\mathbf{B} \tag{1}$$

where dot denotes differentiation with respect to time t, $\mathbf{u}$ is the displacement vector, $\mathbf{J}$ the current density, $\mathbf{J}\times\mathbf{B}$ the Lorentz force and $\mathbf{B}$ is the total magnetic field so that $\mathbf{B} = \mathbf{B}_0 + \mathbf{b}$, $\mathbf{b} = (b_x\ b_y\ b_z)$ is the perturbed magnetic field. The Lorentz force term $\mathbf{J}\times\mathbf{B}$ is included in the displacement equation of motion to incorporate the electromagnetic field

effects. We shall take into account the time independent part of the electro-magnetic body force. Finally, the study of magneto-elastic plane waves will be made within the scope of the linearized theory. We assume that **u, b** and the second order terms on the right-hand side of (1) involving **u, b** and their derivatives are small in order to justify linearization.

In view of the fact that frequencies associated with the vibrations and mechanical waves are much smaller than the frequency of the electro-magnetic waves with the same wave length, the electro-magnetic fields may be regarded as quasi steady. The electro-magnetic fields are governed by the following Maxwell equations with the displacement current and charge density neglected.

$$\nabla \times \mathbf{H} = \mathbf{J} \tag{2a}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{2b}$$

$$\nabla . \mathbf{B} = 0 \tag{2c}$$

where $\mathbf{B} = \mu_e \mathbf{H}$, μ_e is the magnetic permeability and **E** is the electric field.

The generalized Ohm's law is

$$\mathbf{J} = \sigma\left(\mathbf{E} + \frac{\partial \mathbf{u}}{\partial t} \times \mathbf{B}\right) \tag{3}$$

where σ is the electrical conductivity and $\frac{\partial \mathbf{u}}{\partial t}$ is the particle velocity of the medium.

Plane Wave Solutions and Dispersion Relation

We consider the propagation of plane waves in the conducting elastic medium in x–direction so that all field quantities **u, J, b** are proportional to exp $[i(kx-wt)]$ where k is the complex wave number and ω is the real wave frequency. $w/\mathrm{Re}(k)$ then represents the phase velocity of the waves. We write all the field quantities in the form :

$$(\mathbf{u}, \mathbf{J}, \mathbf{b}) = (\mathbf{u}_0, \mathbf{J}_0, \mathbf{b}_0) \exp [i(kx - wt)] \tag{4}$$

Here $\mathbf{u}_0 = (p_0, q_0, r_0)$, $\mathbf{J}_0 = (J_1, J_2, J_3)$, $\mathbf{b}_0 = (b_1, b_2, b_3)$, are amplitude constants.

Further $\mathbf{E} = (E_x, E_y, E_z)$. Equation (2c) leads to $b_x = 0$, while equation (2b) gives

$$\mathbf{E} = \left(E_x \frac{w}{k} b_z, -\frac{w}{k} b_y\right) \tag{5}$$

Equation (2a) implies $\mathbf{J} = \left(0, -\frac{ik}{\mu_e} b_z, \frac{ik}{\mu_e} b_y\right)$ (6)

Further, on linearization, generalized Ohm's law (3) gives

$$J_x = \sigma\left[E_x - iw(qB_3 - rB_2)\right],$$

$$J_y = \sigma\left[\frac{w}{k} b_z - iw(rB_1 - pB_3)\right],$$

$$J_z = \sigma\left[-\frac{w}{k} b_y - iw(pB_2 - qB_1)\right] \tag{7}$$

On elimination of **J** between (6) and (7) and substitution of **u** from (4) into the displacement equation (1), we obtain after linearization, the following five equations in five unknowns p_0, q_0, r_0 and the perturbed quantities b_2, b_3

$$p_0\left[-\rho\omega^2 + (\lambda + 2\mu)k^2 - i\omega k^2(\lambda^1 + 2\mu^1)\right]$$

$$+ \frac{ik}{\mu_e}(b_3 B_3 + b_2 B_2) = 0, \tag{8}$$

$$q_0\left[-\rho\omega^2 + \mu k^2 - \mu^1 i\omega k^2\right] - \frac{ik}{\mu_e} b_2 B_1 = 0, \tag{9}$$

$$r_0\left[-\rho\omega^2 + \mu k^2 - \mu^1 i\omega k^2\right] - \frac{ik}{\mu_e} b_3 B_1 = 0, \tag{10}$$

$$p_0 \sigma i\omega B_3 - r_0 i\sigma\omega B_1 + b_3\left(\frac{ik}{\mu_e} + \frac{\sigma\omega}{k}\right) = 0, \tag{11}$$

$$-p_0 \sigma i\omega B_2 + q_0 \sigma i w B_1 - b_2\left(\frac{ik}{\mu_e} + \frac{\sigma\omega}{k}\right) = 0. \tag{12}$$

Since $b_x = 0$, we set the perturbed and the applied magnetic field such that

$\mathbf{b} = (0, b_2, 0)$ and $\mathbf{B}_0 = (B_1, B_2, 0)$.

Then equations (10) and (11) are automatically satisfied on taking $r_0 = 0$. Equations (8), (9) and (12) then from a system of three homogeneous equations in three unknowns, which lead to the dispersion equation

$$\begin{vmatrix} -\rho\omega^2 + (\lambda + 2\mu)k^2 - (\lambda^1 + 2\mu^1)i\omega k^2 & 0 & \dfrac{ikB_2}{\mu_e} \\ 0 & -\rho\omega^2 + \mu k^2 - \mu^1 i\omega k^2 & -\dfrac{ikB_1}{\mu_e} \\ \sigma i\omega B_2 & -\sigma i\omega B_1 & \dfrac{ik}{\mu_e} + \dfrac{\sigma\omega}{k} \end{vmatrix} = 0 \qquad (13)$$

It follows from the dispersion equation that the significant effects of visco-elastic parameters on the phase velocity $\mathrm{Re}\,(\omega/k)$ are reflected through the terms involving λ' and μ'.

In a non-viscous medium ($\lambda'=\mu'=0$) without thermal effects, the dispersion equation (13) reduces to that of Wilson[9]. Also Paria's[10] results follow from the present analysis when $\lambda'=\mu'=0$, $B_1=0$. Purushothama[11] investigated the propagation of magneto thermo elastic plane waves in the presence of uniform thermal and magnetic field. Although he extended the works of both Wilson and Paria, the results of the present study are consistent with his results in a non-viscosus case with special choices of the angle of orientation of the magnetic field and the thermal effects neglected. In absence of visco-elastic parameters, the dispersion equation (13) also readily agrees with equation (3.24) of Roy Choudhuri and Debnath[6] . However, the dispersion relation (13) gives a fairly general result in the theory of magneto-visco elastic plane waves in infinite media. We introduce the following quantites and the non-dimensional numbers $\sqrt{\dfrac{\lambda + 2\mu}{\rho}} = C_1$-the dilatational wave velocity, $\sqrt{\dfrac{\mu}{\rho}} = C_2$-the shear wave velocity,

$$\sqrt{\frac{\lambda' + 2\mu'}{\rho}} = C_{v_1}, \qquad \sqrt{\frac{\mu'}{\rho}} = C_{v_2},$$

$$R_L = \frac{1}{\rho\mu_e}\frac{B_1^2}{C_2^2}, \quad R_H = \frac{1}{\rho\mu_e}\frac{B_2^2}{C_1^2}$$

where R_H and R_L are non-dimensional pressure numbers, as defined in Pai[12].

$\nu = (\mu_e\sigma\omega)^{-1} = \dfrac{\nu_H}{\omega}$ and $\nu_H = (\sigma\mu_e)^{-1}$ is the magnetic viscosity.

Now introducing $\sigma_i = \omega/c_i$, $i=1, 2$, new quantities, the dispersion equation (13) can be expressed in the following form :

$$\begin{vmatrix} k^2(1 - Mi\omega) - \sigma_1^2 & 0 & \dfrac{ikR_H}{B_2} \\ 0 & (1 - Ni\omega)k^2 - \sigma_2^2 & -\dfrac{ikR_L}{B_1} \\ kiB_2 & -kiB_1 & 1 + i\gamma k^2 \end{vmatrix} \qquad (14)$$

$$\text{where } M = \frac{C_{v_1}^2}{C_1^2} \text{ and } N = \frac{C_{v_2}^2}{C_2^2} \qquad (15)$$

This equation is a more general dispersion equation in the sense that it incorporates the visco-elastic effect on the propagation of coupled waves. This wave may be called coupled magneto-visco elastic dilatational shear wave [following Agarwal[13]]

Expanding the determinant we obtain the equation of degree three in k^2 as

$$(1 + i\gamma k^2)\left[\left\{k^2(1 - Mi\omega) - \sigma_1^2\right\}\left\{k^2(1 - Ni\omega) - \sigma_2^2\right\}\right]$$

$$+k^2\left[k^2(1 - Mi\omega) - \sigma_1^2\right]R_L + k^2\left[k^2(1 - Ni\omega) - \sigma_2^2\right].$$

$$R_H = 0. \qquad (16)$$

This represents a general dispersion relation and shows that if the primary magnetic field has both longitudinal and transverse components, the displacement fields p, q and the perturbed magnetic field b_2 are linked together. It also follows from (16) that the significant effects of visco-elastic parameters on the phase velocity of the waves are reflected through the terms involving M and N. The coupled magneto-visco-elastic waves characterized by the dispersion relation are damped and dispersive.

Infinite Conductivity

In this case, $\sigma \to \infty$ so that v_H tend to zero. The corresponding dispersion relation can be obtained from (16) and has the form

$$k^4\left[(1-Mi\omega)(1-Ni\omega)+(1-Mi\omega)R_L+(1-Ni\omega)R_H\right]$$

$$-k^2\left[\sigma_1^2\{(1-Ni\omega)+R_L\}+\sigma_2^2\{(1-Mi\omega)R_H\}\right]$$

$$+\sigma_1^2\,\sigma_2^2=0. \qquad (17)$$

Thus if the applied primary magnetic field has both longitudinal and transverse components then the longitudinal and transverse components of the displacement field are coupled and modified by both viscosity and electro magnetic field. Both the waves are dispersive and damped. In the case of non-viscous medium ($M = N = 0$), the equation reduces to that of Nowacki[5] and all conclusions of Nowacki can readily be obtained from our analysis.

If the primary magnetic field is absent, that is if $B_1 = B_2 = 0$, so that $R_L = R_H = 0$ the dispersion relation (17) simplifies to

$$\left[k^2(1-Mi\omega)-\sigma_1^2\right]\left[k^2(1-Ni\omega)-\sigma_2^2\right]=0. \qquad (18)$$

In the non-viscous elastic medium ($M=N=0$) the equation (18) becomes

$$\left(k^2-\sigma_1^2\right)\left(k^2-\sigma_2^2\right) = 0. \qquad (19)$$

This corresponds to both the dilatational and the transverse elastic waves. However for viscous medium $(M \neq o,\ N \neq 0)$ the roots of (18) correspond to the dilatational and transverse elastic waves modified by visco-elastic parameters.

If, on the other hand, the primary magnetic field has a non-zero transverse component $R_H \neq 0$, $R_L = 0$, then the dispersion relation (17) simplifies into.

$$\left[k^2\{(1-Mi\omega)+R_H\}-\sigma_1^2\right]\left[k^2(1-Ni\omega)-\sigma_2^2\right]=0. \qquad (20)$$

If $R_H \neq 0$, $R_L = 0$, visco-elastic dilatational wave is perturbed by R_H (electro-magnetic field).

The first factor of equation (20) corresponds to the modified elastic dilatational wave modified by visco-elastic parameters and applied magnetic field R_H [[Quasi-visco-elastic dilatational wave perturbed by electro magnetic field as expected] while the second factor to the modified elastic-shear wave influenced by visco-elastic parameters and unperturbed by electro-magnetic field [Quasi-visco-elastic shear wave unperturbed by electro-magnetic field as expected].

If k_{11} and k_{12} are the roots of the equation (20) then

$$k_{11}^2=\frac{\sigma_1^2}{1+R_H-i\omega M}=a_1+ib_1=R_1\,e^{i\theta_1},$$

$$a_1=\frac{\sigma_1^2(1+R_H)}{(1+R_H)^2+\omega^2M^2}\qquad b_1=\frac{\sigma_1^2\omega M}{(1+R_H)^2+\omega^2M^2}$$

$$k_{11}=\sqrt{R_1}\left(\cos\frac{\theta_1}{2}+i\sin\frac{\theta_1}{2}\right),\quad R_1=\sqrt{a_1^2+b_1^2}$$

and $\tan\theta_1=\dfrac{b_1}{a_1}$.

The modified dilatational wave speed is given by $\dfrac{\omega}{R_e(k_{11})}=\dfrac{\omega}{\sqrt{R_1}\cos\frac{\theta_1}{2}}=$ Quasi-visco-elastic-dilatational wave speed affected by R_H and visco-elastic parameters.

The attenuation co-efficient $\operatorname{Im} k_{11} = \sqrt{R_1}\sin\frac{\theta_1}{2}$.

Similarly, $k_{12}^2 = \frac{\sigma_2^2}{1 - Ni\omega} = a_2 + ib_2 = R_2^{ei\theta_2}$

where $a_2 = \frac{\sigma_2^2}{1 + N^2\omega^2}$, $b_2 = \frac{\sigma_2^2 N\omega}{1 + N^2\omega^2}$,

$$K_{12} = \sqrt{R_2}\left(\cos\frac{\theta_2}{2} + i\sin\frac{\theta_2}{2}\right), \quad R_2 = \sqrt{a_2^2 + b_2^2}$$

and $\tan\theta_2 = \frac{b_2}{a_2}$.

Quasi-visco-elastic shear wave speed is then given by $\frac{\omega}{R_e(K_{12})} = \frac{\omega}{\sqrt{R_2 \cos\frac{\theta_2}{2}}}$ = Quasi-visco-elastic shear wave speed, unaffected by R_H but influenced by visco-elastic parameters.

The attenuation co-efficient $\operatorname{Im} k_{12} = \sqrt{R_2}\sin\frac{\theta_2}{2}$.

Further if the applied magnetic field has a longitudinal component only, $R_H = 0$, $R_L \neq 0$. The dispersion equation (17) reduces to

$$\left\lfloor k^2(1 - Mi\omega) - \sigma_1^2 \right\rfloor \left\lfloor k^2\{(1 - Ni\omega) + R_L\} - \sigma_2^2 \right\rfloor = 0. \tag{21}$$

The first factor corresponds to the modified elastic dilatational wave modified by visco-elastic parameters [Quasi-visco-elastic dilatational wave unperturbed by electro-magnetic field as expected], while the second factor corresponds to the modified elastic shear wave modified by visco-elastic parameters and magnetic field [quasi-visco-elastic shear wave perturbed by electro-magnetic field as expected].

If k_{13} and k_{14} are the roots of the equation (21), $k_{13}^2 = \frac{\sigma_1^2}{1 - Mi\omega} = a_{13} + ib_3 = R_3 e^{i\theta_3}$

where $a_3 = \frac{\sigma_1^2}{1 + M^2\omega^2}, b_3 = \frac{\sigma_1^2 M\omega}{1 + M^2\omega^2}$,

$$K_{13} = \sqrt{R_3}\left(\cos\frac{\theta_3}{2} + i\sin\frac{\theta_3}{2}\right), \quad R_3 = \sqrt{a_3^2 + b_3^2}$$

and $\tan\theta_3 = \frac{b_3}{a_3}$.

Thus the modified dialatational wave speed is given by $\frac{\omega}{\operatorname{Re}(k_{13})} = \frac{\omega}{\sqrt{R_3 \cos\frac{\theta_3}{2}}}$ = Quasi-visco-elastic-dilatational wave speed unaffected by R_L but influenced by visco-elastic parameters.

Here the attenuation co-efficient is $k_{13} = \sqrt{R_3}\sin\frac{\theta_3}{2}$.

Similarly, $k_{14}^2 = \frac{\sigma_2^2}{1 + R_L - Ni\omega} = a_4 + ib_4 = R_4 e^{i\theta_4}$

where

$$a_4 = \frac{\sigma_2^2(1 + R_L)}{(1 + R_L)^2 + \omega^2 N^2}, b_4 = \frac{\sigma_2^2 \omega N}{(1 + R_L)^2 + \omega^2 N^2}$$

$$k_{14} = \sqrt{R_{14}}\left(\cos\frac{\theta_4}{2} + i\sin\frac{\theta_4}{2}\right)$$

where $R_4 = \sqrt{a_4^2 + b_4^2}$ and $\tan\theta_4 = \frac{b_4}{a_4}$.

Quasi-visco-elastic shear wave speed is then given by $\frac{\omega}{\operatorname{Re}(k_{14})} = \frac{\omega}{\sqrt{R_4}\cos\frac{\theta_4}{2}}$ = Quasi-visco-elastic shear wave speed affected by R_L and influenced by visco-elastic parameters.

Here the attenuation co-efficient is

$$\operatorname{Im} k_{14} = \sqrt{R_4}\sin\frac{\theta_4}{2}.$$

If initially the applied magnetic field has both longitudinal and transverse components $(R_H \neq 0, R_L \neq 0)$, the longitudinal and transverse components of displacement vector are coupled and correspond to coupled visco-elastic-dilatational-shear waves modified by electro-magnetic and visco-elastic parameters. Since the roots k_1^2 and k_2^2 of (17) are complex, the coupled magneto-visco-elastic waves are damped and dispersive.

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Bianchi type V cosmological model with stiff fluid

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Abstract

Stiff fluid Bianchi type V tilted cosmological model for perfect fluid distribution in General Relativity, has been investigated. The physical and geometrical aspects of the model are also discussed.

(**Keywords** : stiff fluid/cosmological model/tilted Bianchi type V)

Introduction

The study of stiff fluid cosmological models create more interest as for these models velocity of sound is equal to the velocity of light and its governing equations have the same characteristics as those of gravitational field [(Zel'dovich[1]]. Tabensky and Taub[2] have studied plane symmetric self gravitational fluids with pressure equal to energy density. Wesson[3] has obtained an exact solution to Einstein field with a stiff equation of state. Mohanti *et al.*[4] have investigated cylindrically symmetric Zel'dovich fluid distribution in General Relativity. Bali and Tyagi[5] have investigated stiff magnetofluid cosmological model in General Relativity for perfect fluid distribution in General relativity.

Cosmological models with variable G and L for perfect fluid distribution are investigated by number of authors[6-13].

Bianchi type V models contain isotropic special cases and permit small anisotropy levels at any instant of cosmic time. Homogeneous Bianchi Type V universes representing matter distribution have been studied by Roy and Singh[14,15]. Deo and Karade[16] have investigated that there is a non-existence of Maxwell fields in Bianchi type V model in bimetric relativity.

The orthogonal universes in which the matter moves orthogonally to the hypersurface of homogeneity, have been studied in detail by the above mentioned research workers. But the equations for tilted universe in which the fluid flow is not normal to the hypersurface of homogeneity, are more complicated than those of orthogonal one. These universes necessarily appear inhomogeneous to an observer because in the direction of tilt, he sees a lower density of matter than in the opposite direction as investigated by Gödel[17]. It is due to the fact that the surfaces of instancity do not coincide with the surface of homogeneity.

The general dynamics of tilted models have been studied by King and Ellis[18], Ellis and King[19]. Bradley and Sviestine[20] have investigated that heat flow is expected for tilted cosmological models. The cosmological models with heat flow have been investigated by number of authors[21-28]. The Bianchi type V cosmological models for perfect fluid distribution have been studied by several authors[29-32]. In earlier paper Bali and Meena[33] have investigated conformally flat Bianchi type V tilted cosmological models for perfect fluid distribution in General Relativity.

In this paper, we have investigated stiff fluid type V cosmological model for perfect fluid distribution in General Relativity. To get a determinate solution, we have assumed an extra condition between metric potentials as $A = B^2$. The various physical and geometrical aspects of the models are also discussed.

We consider the Bianchi Type V metric in the form

$$ds^2 = -dt^2 + A^2\, dx^2 + B^2\, e^{2x}\, (dy^2 + dz^2) \qquad (1)$$

where A, B are functions of 't' alone

The energy momentum tensor components for perfect fluid distribution with heat conduction is taken into the form given by Ellis[34] as

$$T_i^j = (\varepsilon + p)\, v_i v^j + p g_i^j + q_i v^j + v_i q^j \tag{2}$$

together with

$$g_{ij}\, v^i\, v^j = -1 \tag{3}$$

$$q_i\, q^j > 0 \tag{4}$$

$$q_i\, v^i = 0 \tag{5}$$

where p is the isotropic pressure, ε the density, q_i the heat conduction vector orthogonal to v^i.

The fluid flow vector has the components $\left(\frac{\sinh\lambda}{A}, 0, 0, \cosh\lambda\right)$ satisfying equation (3) where λ is the tilt angle.

The Einstein's field equations

$$R_i^j - \frac{1}{2} g_i^j = -8\pi T_i^j \tag{6}$$

$$\{c = 1,\ G = 1,\ \Lambda = 0\}$$

for the metric (1) are rewritten as

$$\frac{2B_{44}}{B} + \frac{B_4^2}{B^2} - \frac{1}{A^2} = -8\pi \left[(\varepsilon + p)\sinh^2\lambda + p + 2Aq'\sinh\lambda\right] \tag{7}$$

$$\frac{A_{44}}{A} + \frac{B_{44}}{B} + \frac{A_4 B_4}{B} - \frac{1}{A^2} = -8\pi p \tag{8}$$

$$2\frac{A_4 B_4}{AB} + \frac{B_4^2}{B^2} - \frac{3}{A^2} = -8\pi \left[-(\varepsilon + p)\cosh^2\lambda + p - 2Aq'\sinh\lambda\right] \tag{9}$$

$$2\frac{A_4}{A} - \frac{2B_4}{B} = -8\pi\left[(\varepsilon + p)A\sinh\lambda\cosh\lambda + A^2 q'(\cosh\lambda + \sinh\lambda\tanh\lambda)\right] \tag{10}$$

where the suffix '4' after A, B denotes ordinary differentiation with respect to t.

Equation (7) – (10) are four equations in six unknowns A, B, ε, p, q and λ.

For the complete determination of these quantities, we use the stiff fluid condition

$$\varepsilon = p \tag{11}$$

and the other condition

$$A = B^2 \tag{12}$$

as given in introduction.

From equations (7) and (9), we have

$$\frac{B_{44}}{B} + \frac{A_4 B_4}{AB} + \frac{B_4^2}{B^2} - \frac{2}{A^2} = 4\pi(\varepsilon - p) \tag{13}$$

Equations (11), (12) and (13) lead to

$$\frac{B_{44}}{B} + 3\frac{B_4^2}{B^2} - \frac{2}{B^4} = 0 \tag{14}$$

From equations (7), (8), (9), (11) and (12), we have

$$2\frac{B_4^2}{B^2} - \frac{B_{44}}{B} - \frac{2}{B^4} = 8\pi p\cosh 2\lambda + 16\pi A q'\sinh\lambda \tag{15}$$

Equations (10), (11), (12) and (15) lead to

$$\frac{B_{44}}{B} - 2\frac{B_4^2}{B^2} + \frac{1}{B^4} = \left(3\frac{B_{44}}{B} + 4\frac{B_4^2}{B^2} - \frac{1}{B^4}\right) \frac{1}{\cosh 2\lambda} + 2\frac{B_4}{B}\frac{\tanh 2\lambda}{B^2} \tag{16}$$

From equation (14), we have

$$B f f' + 3f^2 = 2B^{-2} \tag{17}$$

where $B_4 = f(B)$.

Equation (17) leads to

$$2 f f' + \frac{6}{B} f^2 = \frac{4}{B^3} \tag{18}$$

which again leads to

$$\frac{d}{dB}\left(f^2\right) + \frac{6}{B} f^2 = \frac{4}{B^3} \tag{19}$$

Its solution is given by

$$f^2 = \frac{B^4 + l}{B^6} \tag{20}$$

where l is constant of integration and $f = \frac{dB}{dt}$. From equation (20), we have

$$\frac{B^3}{\sqrt{B^4 + l}} dB = dt \tag{21}$$

Equation (21) leads to

$$B^4 = [(2t + m)^2 - l] \tag{22}$$

where l and m are constants of integration.

Thus, after the suitable transformation of coordinates, the metric (1) reduces to the form

$$ds^2 = -\frac{dT^2}{4} + \left(T^2 + \beta\right) dX^2 + \sqrt{\left(T^2 + \beta\right)}$$

$$e^{2X}\left(dY^2 + dZ^2\right) \tag{23}$$

where $2t + m = T$ (24)

Some Physical and Geometrical Features

The pressure and density for the model (23) are given by

$$8\pi p = 8\pi \varepsilon = \frac{5l}{\left(T^2 - l\right)^2} \tag{25}$$

The tilt angle λ is given by equation (16) which leads to

$$\left(\frac{B_{44}}{B} - \frac{2B_4^2}{B^2} + \frac{1}{B^4}\right)\cosh 2\lambda = \frac{2}{B^2}\frac{B_4}{B}$$

$$\sinh 2\lambda - \left(\frac{3B_{44}}{B} + \frac{4B_4^2}{B^2} - \frac{1}{B^4}\right) \tag{26}$$

Using (22) in (26), we have

$$\cosh 2\lambda = \frac{\left(30l^2 + 20lT^2\right) \pm 16\sqrt{l}T\sqrt{-\left(T^2 - l\right)^2}}{18l^2 + 32lT^2} \tag{27}$$

$\cosh 2\lambda$ is defined only when $T^2 = l$. Thus using $T^2 = l$ in (27), we have

$$\cosh 2\lambda = 1$$

which leads to

$$\cosh \lambda = 1 \tag{28}$$

which implies that $\lambda = 0$.

The reality conditions given by Ellis[35] as

(i) $(\varepsilon + p) > 0$ (ii) $\varepsilon + 3p > 0$, leads to $l > 0$. (29)

The expansion θ calculated or the flow vector v^i is given by

$$\theta = \frac{\partial}{\partial t}(\cosh \lambda) + \frac{2 \sinh \lambda}{A} + \cosh \lambda \left(H_1 + 2H_2\right)$$

where H_1 and H_2 are components of Hubble parameters in x and y directions.

Thus,
$$\theta = \frac{4T}{T^2 - l} \tag{30}$$

The non-vanishing components of shear tensor (σ_{ij}) and rotation tensor (ω_{ij}) are given by

$$\sigma_{11} = A^2 H_1 \cosh\lambda - \frac{1}{3}\theta A^2 \cosh^2\lambda$$

$$+A\sinh\lambda\cosh\lambda\frac{\partial v_1}{\partial t}$$

$$= \frac{2T}{3} \tag{31}$$

$$\sigma_{22} = \frac{B^2}{A}e^{2z}\sinh\lambda + \cosh\lambda\, B^2 e^{2x} H_2 - \frac{1}{3}\theta B^2 e^{2x}$$

$$= -\frac{T e^{2x}}{3\sqrt{T^2 - l}} = \sigma_{33} \tag{32}$$

$$\sigma_{44} = -\sinh^2\lambda\frac{\partial v_4}{\partial t} - \frac{1}{3}\theta\sinh^2\lambda$$

$$+(H_1)\sinh^2\lambda\cosh\lambda = 0 \tag{33}$$

$$\sigma_{14} = -\sinh^2\lambda\frac{\partial v_1}{\partial t} + \frac{1}{3}\theta\, A\sinh\lambda$$

$$\cosh\lambda - (H_1)\, A\sinh\lambda - W_{14} == 0 \tag{34}$$

$$W_{14} = \frac{1}{2}\left[\sinh^2\lambda\frac{\partial v_1}{\partial t} + (H_1)\, A\sinh^3\lambda\right.$$

$$\left. -\frac{\partial v_4}{\partial t} A\sinh\lambda\cosh\lambda\right] = 0 \tag{35}$$

The expressions for fluid velocity vector v^1 and v^4 and heat conduction vector q^1 and q^4 are given by

$$v^1 = \frac{\sinh\lambda}{A} = 0 \tag{36}$$

$$v^4 = \cosh\lambda = 1 \tag{37}$$

$$q^1 = 0 \tag{38}$$

$$q^4 = 0 \tag{39}$$

The rates of expansion H_i in the direction of *X*, *Y*, *Z*-axes are given by

$$H_1 = \frac{A_4}{A} = \frac{2T}{\left(T^2 - l\right)} \tag{40}$$

$$H_2 = H_3 = \frac{B_4}{B} = \frac{T}{T^2 - l} \tag{41}$$

Discussion

The model (23) possesses big bang type singularity at $T = \sqrt{l}$ i.e. at the cosmic time $n = \sqrt{T^2 - l}$. When $T \to \sqrt{l}$ then $\theta \to \infty$. There is a singularity in the model at cosmic time n=0 i.e. at $T = \sqrt{l}$. When $T \to \sqrt{l}$ then $\in \to \infty$. The model (23) in general represents shearing, non-rotating and non-tilting universe. Since $\lim_{T \to \infty} \frac{\sigma}{\theta} \neq 0$. Hence the model does not aproach isotropy for large values of *T*. When $T \to \sqrt{l}$ then coshλ = 1 which leads to λ = 0. Thus the model (23) represents non-titled model at $T = \sqrt{l}$.

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A theoretical study of specific heat at constant volume for liquid metals and its temperature dependence

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Abstract

This work presents a simple formalism for specific heat at constant volume (C_v) and its temperature dependence for liquid metals. Both the characteristic features of the liquid phase *viz.* the short-range spatial order and significant temporal disorder have been incorporated in the development of the formalism i.e. all three types of motions *viz.* contributions due to the vibrational motion of ion-cores about their pseudo-equilibrium positions, due to the valence electrons and diffusional motion of atoms from one pseudo-equilibrium position to the other have been considered. The calculated values of C_v for sodium, potassium, rubidium and mercury in liquid phase over a wide range of temperature ($T_m - T_b$) agree well with the available experimental data. Maximum deviation of the calculated values from the experimental data for Na, K, Rb and Hg are 6.5%, 9.9%, 5.6% and 6.0% respectively, which are well within the experimental uncertainties.

(**Keywords** : liquid theory/specific heat at constant volume/ liquid metals/short-range-order/temporal disorder)

Introduction

The existence of topological short-range-order (TSRO) in liquid metals has been stressed by many theorists and it is also established through X-ray and neutron diffraction studies[1–2]. But, a very few attempts have been made to develop a formalism for the variation of TSRO with temperature and its correlation with bulk properties[2,3] which may lead to a self–consistent and unified formalism for this state of matter. With this objective, recently authors have developed a statistical theory for simple liquids[4], which has been used to study the temperature dependence of the TSRO parameter[5-8] and a number of equilibrium and transport properties such as average coordination number[6, 8], coefficient of surface tension[4], coefficient of self-diffusion[9-11], coefficient of viscosity[10], coefficient of thermal conductivity[7,9] and specific heat[11] for inert liquids. The temperature dependence of three transport coefficients ratio numbers *viz.* Schmidt number, Prandtl number and Eucken factor for inert liquids have been explained successfully through these formalisms[10]. A simple formalism has also been deduced for the entropy of melting[12]. It is found that the calculated values of these properties agree well with the available experimental values over a wide range of temperatures for a number of liquids.

Various theoretical models have been proposed to study the heat capacities of metallic liquids, none has been successful because the motion of atoms in the liquid state is extremely complex and generally the proposed models overestimate, underestimate or neglect some of the contributions. Moreover, no empirical relationship has been successful in providing reliable estimates of liquid metal heat capacities[1,13]. Therefore, in the present work, effort is made to develop a simple formalism for the temperature dependence of specific heat at constant volume for metallic liquids. The calculated values of C_v for sodium, potassium, rubidium and mercury in liquid phase over a wide range of temperature agree well with the available experimental data.

Theory

Topological-short-range-order (TSRO) and its variation with temperature

A careful analysis of the atomic distribution functions (ADF) obtained from the experimental X-

ray or neutron diffraction studies for a number of liquids at different temperatures reveals the following features of liquid metal phase[1,14,15]. In spite of increase in the bulk volume on melting (around 2% to 6% for metallic elements) the most probable separation among the atoms in the liquid phase remains almost the same as it is in the corresponding crystalline phase. As against this, there is a considerable decrease in the average coordination number. With the further increase in temperature the bulk volume goes on increasing; both the short-range-order (SRO) and the average coordination number decrease gradually but there is hardly any change in the most probable separation among the atoms. ADF curves also indicate a continual exchange of atoms among the neighbouring shells.

In view of these aspects the authors have developed a simple statistical theory for metallic liquids. According to the proposed theoretical formalism, any liquid metal can be viewed as a system consisting of a large number of cores (which include nucleus and all inner electrons) and free electrons (almost all or a fraction of valence electrons act as free electrons) which at any instant of time are members of one or the other short-range-ordered (SRO) micro-regions with micro-voids in between. These free electrons move under the influence of potential caused by all ion-cores within the ordered micro-region and the self field. The motion of ion-core in the self field and of electron gas can be described in terms of two types of motion. One, the vibrational motion of the reference ion-core about its pseudo-equilibrium position and second, the exchange of these pseudo-equilibrium positions by diffusion.

Just on the melting there is hardly any change in the most probable separation among the atoms and the increase in bulk volume is also very small. Therefore, for the proposed system, enthalpy of fusion L_m can be viewed as the increase in the surface energy due to the transformation of long-range order system into the short-range ordered regions i.e.

$$L_m = dU = \sigma_m \; K \; \Delta \; S. \qquad (1)$$

where dU is the total change in the internal energy of the system, σ_m is the free surface energy per unit area, constant K depends upon the intrinsic nature of the element particularly electronic configuration and ΔS is the difference in the ensemble average surface area of all the micro-regions in the liquid phase and the total surface area in the parent crystalline phase at the melting temperature.

At any instant of time, let $n_1, n_2, \ldots\ldots, n_n$ be the number of micro-regions having sizes r_1, $r_2, \ldots\ldots, r_n$, respectively then the total surface area of all the micro-regions at that instant of time is $\sum_{i=1}^{n} k_{si} r_i^2 n_i$, where k_{si} is the surface shape factor of i^{th} micro-region, e.g. it would be 4π if it is spherical in shape. On account of significant temporal disorder the local arrangement of cores around any point keeps on changing with time i.e. the values of k_{si}, n_i and r_i are changing continuously. Let us consider an ensemble whose members represent conditions of this system at different instant of time. Let the ensemble average surface area of all the micro-regions be represented as $\left\langle \sum_{i=1}^{n} k_{si} r_i^2 n_i \right\rangle$. Since the system is in the thermal equilibrium, this ensemble average surface area and hence the total surface energy are constrained by the enthalpy of fusion i.e. these remain constant with time. Therefore, equation (1) can be written as

$$L_m = \sigma_m K \left[\left\langle \sum_{i=1}^{n} k_{si} r_i^2 n_i \right\rangle - 4\pi \left(\frac{3V_S}{4\pi} \right)^{2/3} \right]. \qquad (2)$$

where V_S is the molar volume in the crystalline phase and the second term at the right hand side in equation (2) is the surface area in the crystalline phase at the melting temperature. Further, the increase in volume is assumed to be uniformly distributed among the micro-regions as micro-voids i.e.

$$\left\langle \sum_{i=1}^{n} k_{vi} r_i^3 n_i \right\rangle = V_S \qquad (3)$$

where k_{vi} is the volume shape factor of i^{th} microregion, it would be $(4\pi/3)$ for spherical shape. Now the extent of TSRO at the melting r_m and that at any temperature r are defined as the ensemble

average lengths up to, which the short-range-order persists in the liquid phase at the melting temperature T_m and at any temperature T, respectively. Again, r_m is defined through the following equation

$$\left\langle \sum_{i=1}^{n} k_{si} r_i^2 n_i \right\rangle = 4\pi \left[\frac{3V_S}{4\pi r_m^3} \right] r_m^2 . \tag{4}$$

Using equation (4), equation (2) can be written as

$$L_m = \sigma_m K \left[4\pi r_m^2 \left(\frac{3V_S}{4\pi r_m^3} \right) - 4\pi \left(\frac{3V_S}{4\pi} \right)^{2/3} \right] . \tag{5}$$

Since the extent of the short-range-order is very small, in equation (5) the contribution of second term is about 10^{-8} times the first term for liquid metals, hence the second term is neglected.

A dimensionless parameter, x, which is the quantitative measure of the topological-short-range-order, is defined as the ratio (r/a), where $a=((3V_S)/(4\pi N))^{1/3}$ is the radius of the space available to an atom in the crystalline phase just at the melting temperature. Accordingly, the TSRO parameter at the melting is $x_m = (r_m/a)$. Using equation (5), x_m can be expressed as[4]

$$x_m = \left(36\pi V_S^2 N \right)^{1/3} \frac{\sigma_m K}{L_m} . \tag{6}$$

Again above the melting temperature, the energy given to the system ΔE_L can be viewed as the sum of increase in vibrational energy of ion-cores ΔE_{vib}, diffusional energy of atoms ΔE_{diff} and valence electron energy ΔE_{el} i.e. $\Delta E_L = \Delta E_{vib} + \Delta E_{diff} + \Delta E_{el}$. To obtain the vibrational contribution, the authors have used Einstein's distribution function for the assembly of oscillators along with the constraint put by TSRO on the allowable wavelength of collective oscillations. Accordingly, it is shown that vibrational energy can be expressed as[4]

$$E_{vib} = \int_{\nu_o}^{\nu_m} \frac{12 h \pi V_S \nu^3}{\bar{u}^3 \left(exp(h\nu / k_B T) - 1 \right)} d\nu \tag{7}$$

$$\text{with } \nu_o = \left(\frac{9}{16\pi^2} \right)^{1/3} \frac{\bar{u}}{r} \text{ and } \nu_m = \left(\frac{9}{16\pi^2} \right)^{1/3} \frac{\bar{u}}{a} \tag{8}$$

where $\bar{u}$ is the average velocity of the collective modes. ν_0 and ν_m are minimum and maximum allowable frequencies of collective oscillations.

Increase in vibrational energy ΔE_{vib} is also related to TSRO parameter x as[4]

$$\Delta E_{vib} = \frac{-3\sigma_m K V_S}{a x^2} \Delta x. \tag{9}$$

Using above equations, following expression[4] is obtained for the TSRO parameter x

$$\frac{1}{x^3} + \frac{4\pi\sigma_m K a^2}{3k_B T x} - \left[\left(1 - \frac{T_m}{T} \right) + \frac{T_m}{T} \left(\frac{1}{x_m^3} \right) + \frac{4\pi\sigma_m K a^2}{3k_B T x_m} \right] = 0. \tag{10}$$

The solution of equation (10), that is, the value of x at any temperature T can be obtained using Cardano's formula. In fact, the TSRO parameter is the most useful quantity as expressions for various equilibrium and transport properties have been deduced in terms of x.

Specific Heat at Constant Volume and its Temperature Dependence

The specific heat at constant volume C_V for liquid metals consists of a contribution from the cores plus the contribution from the free electrons. For metallic liquids C_V can be expressed as $C_V = (dE/dT)_V$, where $E_L = E_{vib} + E_{diff} + E_{el}$ is the total internal energy of the system.

(i) *Vibrational contribution to the specific heat*: The expression for ΔE_{vib} can be deduced through equations (7-9) in a straightforward manner as shown in our earlier work[11] as

$$\Delta E_{vib} = 3Nk_B \left[1 - \frac{1}{x^3} + \frac{3T}{x^3} \cdot \frac{\left(1 - x^3\right)}{\left(3T + bx^2\right)} \right] \Delta T. \tag{11}$$

Accordingly, following expression has been obtained for vibrational contribution to the specific heat (C_{Vvib})[11].

$$C_{V_{vib}} = 3Nk_B\left[1-\frac{1}{x^3}+\frac{3T}{x^3}\cdot\frac{(1-x^3)}{(3T+bx^2)}\right] \quad (12)$$

where $b = ((4\pi\sigma_m Ka^2)/(3k_B))$.

(ii) Diffusional contribution to the specific heat: According to proposed model of liquid state, the probability of diffusional displacement at any instant of time is not the same for all ion-cores, only ion-cores on the surface of any micro-region, named superficial ion-cores now onwards have significantly large probabilities for this event. Each superficial core performs more or less large number of oscillations about a pseudo-equilibrium position, during a certain time t_1 before undergoing the diffusional displacement, which is the next pseudo-equilibrium position and is at a distance l, of the order of $(((V-V_S)/N)^{1/3}\ .x)$. Here l can also be viewed as effective mean free path for the superficial ion-core. The simplest prescription for the potential energy of a superficial ion-core, as it moves from the surface of one ordered micro-region to the other can be taken as a flat-top potential energy barrier separating two equivalent potential energy wells. The ratio of probabilities of finding a core in the micro-void region and on the surface of an ordered micro-region would be[11]

$$\frac{P_2}{P_1}=\frac{l}{a}exp\left(-\overline{U}_s / k_BT\right) \quad (13)$$

with $P_1+P_2 = 1$. Here $\overline{U}_S$ is ensemble average potential energy of the superficial core for all possible configurations for a given value of x. Further, in a metallic system, the valence electrons of a core are shared by all neighbours so long as a core is within any SRO region and is performing vibrational motion, when a core leaves the surface of any SRO region, due to strong electrostatic interaction, it picks up its electron and diffuses as a pseudo atom. Accordingly, diffusional energy of atoms (E_{diff}) can be written as

$$E_{diff}=\frac{3}{2}P_2\,N\,k_B\,T. \quad (14)$$

Using equations (13) and (14) diffusional contribution of atoms to the specific heat $(C_{V_{diff}})$ can be obtained as

$$C_{V_{diff}}=\frac{3\,N k_B\,P_2}{2}\left(1+P_1\left(\frac{(1-x^3)\,T}{(3T+bx^2)}+\frac{\overline{U}_S}{k_BT}\right)\right) \quad (15)$$

(iii) Electron contribution to the specific heat: The electron contribution to the specific heat can be deduced considering the fact that in liquid phase the valence electrons of the atoms are free but are still confined within SRO regions formed by cores of nearest neighbour cage. Within the ordered micro-region the free electron density is quite high. This electron gas is in the uniform background of positive ion-cores. Using quantum model of the free electron gas along with Fermi-Dirac statistics, the expression for electron energy per mole (E) can be expressed in the way analogous to the one used for metals in crystalline phase as

$$E=\frac{3}{5}N\mu_0'\left[1+\frac{5\pi^2}{12}\left(\frac{K_BT}{\mu_0'}\right)^2 -\frac{\pi^4}{16}\left(\frac{k_BT}{\mu_0}\right)^4+\ldots\ldots\ldots\right] \quad (16)$$

where $\mu_0'=(\mu/f), \mu_0$ is the Fermi energy of the element in crystalline phase and f is a constant whose value would depend on the electronic configuration of core. In fact equation (16) indicates that due to the small extent of ordered micro-regions, the characteristic energy of liquid phase gets modified by a factor f. Accordingly, neglecting the higher order terms electron heat capacity per mole (C_{vel}) can be written as

$$C_{V_{el}}=\frac{\pi^2\,N\,k_B^2\,T}{2(\mu_0/f)} \quad (17)$$

Hence the total specific heat of a metallic liquid becomes

$$C_V = 3Nk_B\left[\left(1-\frac{1}{x^3}\right)+\frac{3T\left(1-x^3\right)}{x^3\left(3T+bx^2\right)}\right]+\frac{3Nk_BP_2}{2}\cdot$$

$$\left[1+P_1\left\{\frac{\left(1-x^3\right)T}{\left(3T+bx^2\right)}+\frac{\overline{U}_S}{k_BT}\right\}\right]+\frac{\pi^2Nk_B^2T}{2(\mu_0/f)}. \quad (18)$$

Table 1 – Comparison of calculated and experimental values of specific heat at constant volume of liquid metals.

Temp. T (K)	Specific heat at constant volume C_v(J/mole K)					% Dev.
	Cv_{vib}	Cv_{diff}	Cv_{el}	Cv_{calcd}	Cv_{exptl}	
			Sodium			
371	24.46	1.34	2.31	28.11	30.08	-6
400	24.11	1.80	2.49	28.40	29.44	-3
500	22.08	2.81	3.11	28.00	27.34	2
600	19.14	3.53	3.74	26.40	25.55	3
700	16.00	4.12	4.36	24.48	24.03	2
800	13.18	4.63	4.98	22.79	22.79	0
900	10.85	5.06	5.60	21.51	21.80	-1
1000	8.99	5.42	6.23	20.64	21.07	-2
1100	7.52	5.73	6.85	20.10	20.57	-2
1200	6.36	6.00	7.47	19.83	20.29	-2
1300	5.43	6.23	8.09	19.75	20.22	-2
1400	4.69	6.43	8.72	19.84	20.31	-2
1500	4.08	6.62	9.34	20.03	20.56	-2
1600	3.58	6.78	9.96	20.32	20.92	-3
1700	3.17	6.93	10.58	20.68	21.37	-3
1800	2.82	7.07	11.21	21.10	21.86	-3
1900	2.52	7.20	11.83	21.56	22.31	-3
2000	2.27	7.33	12.45	22.05	22.66	3
			Potassium			
337	24.42	1.42	2.82	28.65	28.46	1
400	23.32	2.32	3.34	28.98	27.32	6
500	20.40	3.21	4.18	27.79	25.83	7
600	16.87	3.90	5.02	25.79	24.69	4
700	13.59	4.48	5.85	23.93	23.89	0
800	10.92	4.97	6.69	22.57	23.43	-4
900	8.84	5.37	7.52	21.73	23.27	-7
1000	7.25	5.71	8.36	21.31	23.40	-9
1050	6.59	5.85	8.78	21.22	23.57	-10
			Rubidium			
313	24.36	1.35	3.23	28.93	29.29	-1
350	23.68	1.90	3.61	29.19	28.75	1
400	22.31	2.46	4.13	28.90	28.04	3
500	18.59	3.36	5.16	27.10	26.72	1
600	14.73	4.10	6.19	25.01	25.55	-2
700	11.52	4.72	7.22	23.46	24.50	-4
800	9.08	5.22	8.25	22.55	23.57	-4
900	7.26	5.64	9.28	22.18	22.74	-2
1000	5.91	5.98	10.32	22.20	21.98	1
1100	4.88	6.27	11.35	22.50	21.30	6
			Mercury			
234	24.78	0.19	0.51	25.48	25.23	1
273	24.57	0.38	0.60	25.55	24.73	3
350	23.80	0.94	0.76	25.50	24.06	6
450	22.00	1.78	0.98	24.76	23.60	5
550	19.53	2.57	1.20	23.30	23.14	1
630	17.37	3.11	1.37	21.86	22.39	-2

Results and Conclusion

Calculations have been made for liquid metals (Na, K, Rb and Hg) over a wide range of temperatures. The input parameters have been taken from literature[16-18]. To determine TSRO parameter x at any temperature, we found that the value of K is 0.32 for alkali metals (Na, K, Rb) and is 0.23 for mercury. The estimation of $\overline{U}_S$ is the most complicated task since it is the ensemble averaged barrier energy of superficial cores. It is expected that $\overline{U}_S$ should be some fraction of cohesive energy E_S i.e. $\overline{U}_S=E_S/y$. Here y has been evaluated empirically for the best
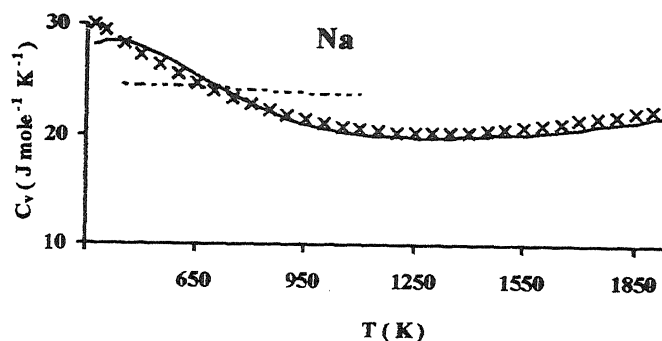
Fig. 1 – Variation of specific heat (C_V) with temperature (T) for liquid sodium. x exp. values, ... calcd. values using significant structure theory and —— present calcd. values.
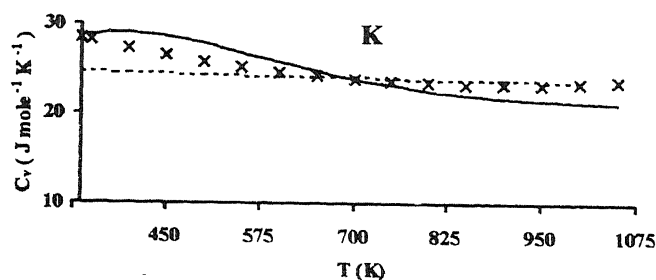
Fig. 2 – Variation of specific heat (C_V) with temperature (T) for liquid potassium. x exp. values, ----- calcd. values using significant structure theory and —— present calcd. values.
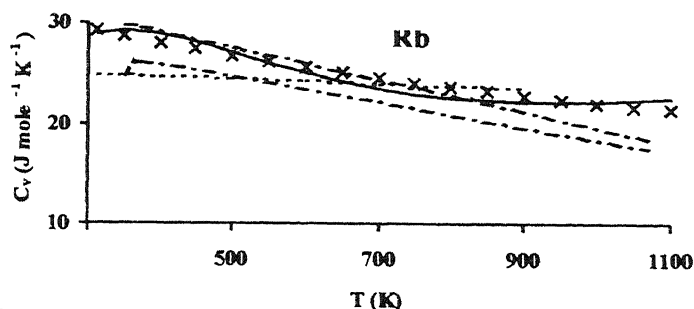
Fig. 3 – Variation of specific heat (C_V) with temperature (T) for liquid rubidium. x exp. values, ... calcd. values using molecular dynamics, ---- calcd. values using significant structure theory and —— present calcd. values.
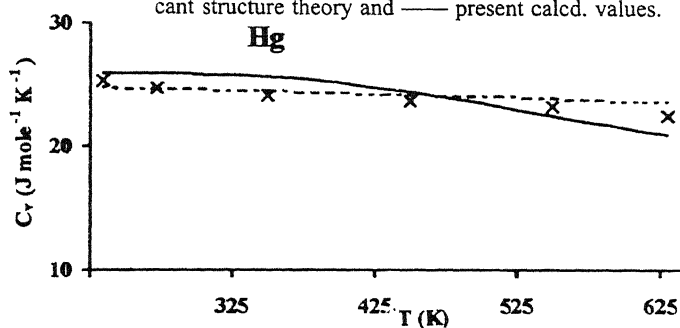
Fig. 4 – Variation of specific heat (C_V) with temperature (T) for liquid mercury. x exp. values, ... calcd. values using significant structure theory and —— present calcd. values.

fit, the value of y for sodium, potassium and rubidium is 8.0 and for mercury, it is 4. Here empirical constant f is 4.25 for Na, K, Rb and Hg. We would like to stress that the same values of K, x versus T and $\overline{U}_S$ have been used to explain a number of other properties *viz.* surface tension, self-diffusion, viscosity and Schmidt number. The calculated and experimental values of C_V are given in Table 1. In this table vibrational, diffusional and electron contribution to specific heat are shown in column 2,3,4 respectively. A careful study of these contributions reveal that in the temperature region near melting due to considerable extent of short-range-order i.e. strong spatial correlation the vibrational contribution is almost 3R, with the rise in temperature as the SRO gradually decreases this contribution decreases gradually and becomes ~ R for Na, K and Rb at normal boiling temperature. It is interesting to see that due to high potential energy mercury has higher value of vibrational contribution at melting and it decreases to ~ 2R at boiling. For these liquids the diffusional contribution is very small near melting and with the rise in temperature as the temporal disorder increases the diffusional contribution increases. For Na, K and Rb it is ~ .7 R near boiling whereas for mercury due to higher potential energy this contribution is much less ~ .4R at normal boiling. Similarly electron contribution is also very small near melting and increases with the rise in temperature as per equation (17). Further electron contribution for Hg is much less than alkali. This is consistent with the fact that even in crystalline phase the Fermi energy of Hg is of the order of a magnitude higher than the values of Fermi energy of alkali elements. All of the above mentioned aspects are consistent with the expected behaviour of specific heat of metallic liquids and its dependence on temperature. Experimental studies of C_V for metallic elements in liquid phase reveal that for liquid Na, K, Rb and Hg total specific heat is significantly more than 3R (~3.1R to 3.6R) at melting[1,19]. It decreases with the rise in temperature to around 2.5R(2.4R–2.8R) up to the boiling temperature above which it starts increasing again, although with a very low slope i.e. a broad depression valley is seen in the trends of C_V. Present calculated values along with calculated values as reported by Breitling and Eyring[20] using significant structure theory and Nowotny *et. al.*[21] using molecular dynamics and experimental values[19] are also plotted

in Fig. (1-4). It is evident from these figures that agreement between present calculated values with experimental values is better than other calculated values which do not depict even correct trend. Maximum deviation of the present calculated values from the experimental data for Na, K, Rb and Hg are 6.5%, 9.9%, 5.6% and 6.0%, respectively which are well within the experimental uncertainties.

The theoretical study also indicates a little increase (0.3% to 1.1%) in the values of C_V just above the melting, which is perhaps missed in experimental measurements. The proposed theory explains successfully all these observations and provides a formalism, which predicts both the values at the melting as well as the whole trend with temperature correctly. Thus the proposed approach may be considered as a unified novel approach to understand behaviour of elements in liquid phase.

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Quercetin-3-O-α-L-rhamnopyranoside from the seeds of *Trigonella foenum-graecum*

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Abstract

Quercentin-3-O-α-L-rhamnopyranoside (SA-IV) has been isolated from the seeds of *Trigonella foenum-graecum* (N.O. Leguminosae). SA-IV analysed for m.f. $C_{21}H_{20}O_{11}$, m.p. 226-229°C and [M*] 448 (EIMS) by various spectral analysis and chemical degradation.

(**Keywords :** chemical degradation/*Trigonella foenum-graecum*/ Leguminosae/seeds/glycoside/L-rhamnose).

The plant *Trigonella-graecum* (N.O. Leguminosae) is found through out India[1-3]. Different parts of this plant are used in dropsy, chronic cough, heart diseases, piles, vomiting, bronchitis, diabetes, preventing of falling of hairs, external swellings and burns. Earlier workers have reported the presence of furostanol saponins, sapogenin, diosgenin, yamogenin, tigogenin and 4-hydroxy isoleucine in its seeds[4-9]. This work shows that the seeds of *Trigonella foenum-graecum* also contain flavoneglycoside like quercetin-3-O-α-L-rhamnopyranoside.

The seeds of *Trigonella foenum-graecum* were collected locally and identified by reputed taxonomist. Analytical thin layer and column chromatography were performed on silica gel. Whatman filter paper no. 1 was used for paper chromatography. Butanol : acetic -acid : water [(BAW) 4:1:5] was used as solvent system and aniline hydrogen phthalate as visualising agent in the paper chromatography of sugars. ^{13}C-NMR, ^{1}H-NMR and mass spectra were recorded at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. DMSO solvent was used for ^{1}H-NMR and ^{13}C-NMR studies. Melting points were determined on a Biochem melting point apparatus in open capillary. The reagents were supplied by Goldie Lab Chem, Mumbai.

Isolation : About 2.0 kg of air dried and powdered seeds of *Trigonella foenum-graecum* were defatted with petroleum ether (60-80°C) and extracted with aqueous MeOH. The MeOH extract was concentrated under reduced pressure. The resultant syrupy mass was extracted with water. The water-soluble part was successively extracted with benzene, chloroform and ethyl acetate. The ethyl acetate extract when worked up provided yellow crystalline compound SA IV, which displayed single spot on TLC (solvent system EtOAc : Ac_2O : AcOH : H_2O 5:3:1:1) and was crystallised from methanol.

SA-IV analysed for m.f. $C_{21}H_{20}O_{11}$, m.p. 226-229°C and [M$^+$] 448 (EIMS). SA-IV responded to all the characteristic colour reactions of flavonoids[10-11] and also gave positive Molisch's Test for glycoside.

Acid hydrolysis of the glycoside SA-IV : Glycoside SA-IV (0.25g) was hydrolysed with 30 mL of 7% H_2SO_4. The ethereal layer when worked up yielded yellow crystals of aglycone SA-IV (A) which analysed for m.f. $C_{15}H_{10}O_7$, m.p. 318-320° and [M$^+$] 302 (EIMS), [Found C = 59.52%, H = 3.31%; calculated C = 59.60%, H = 3.31%]. The aglycone SA-IV (A) responded to all characteristic colour reaction of flavonoid and was identified as quercetin by comparison of its spectral data[12-17] with flavonoids. The sugar moiety in the aqueous hydrolysate was identified as L-rhamnose by paper chromatography.

Permethylation[18] followed by hydrolysis of glycoside-SA-IV : Glycoside SA-IV (0.04g) was treated with methyl iodide (5mL) and Ag_2O (0.02g) in DMF (5 mL) in a conical flask (250 mL). The reaction mixture was left for about 48h at room temperature. The precipitate so obtained when worked-up and analysed by paper chromatography was found to contain 2, 3, 4 tri-O-methyl-L-rhamnose, which showed that C_1 of L-rhamnose was involved in the glycosydation.

Enzymatic hydrolysis of SA-IV : The glycoside SA-IV (0.03g) was dissolved in ethanol (10 mL) and mixed with (0.025g) of takadiastase (Goldie Lab Chem, Mumbai) in a conical flask. The contents were allowed to stand for 8h at room temperature and then filtered. The aglycone was identified as quercetin by superimposable spectral analysis. The sugar in the hydrolysate was identified as L-rhamnose by paper chrmatography confirming that C-3 OH of the aglycone was linked to C-1" of L-rhamnose through α-linkage.

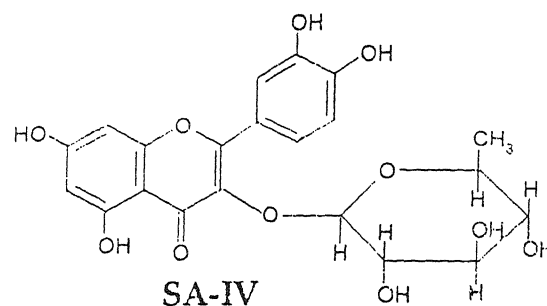
Periodate oxidation of SA-IV : The glycoside SA-IV (0.05g) was dissolved in methanol (40 mL) in a conical flask (100 mL) fitted with a glass stopper. Sodium meta periodate (15 mL) was added and the reaction mixture was left for 48h. Simultaneously a blank experiment was run with the same procedure. The amount of sodium meta periodate consumed and formic acid liberated was estimated by Jone's method. The results showed that one mole of glycoside (SA-IV) required 2.05 moles of periodate and liberated 1.05 moles of formic acid indicating that the sugar was in pyranose form in SA-IV.

Its IR. spectrum showed absorption bands at ν_{Max}^{KBr} cm^{-1} 3399.4 (OH), 2927.9 (C-H stret.), 1640.8 (>C=O), 1387.7 (C-O-C bending), 1053.4, 1387.7-1053.4 (O-glycoside).

^{1}H NMR spectrum of SA-IV showed signals at δ 7.74 (s, H-2'), δ 7.56 (d, *J*=8.2 Hz, H-6') and δ 6.92 (*d*, *J*=8.1 Hz, H-5') protons of ring B, and doublets at δ 6.27, δ 6.39 attributable to the C-6 and C-8 protons. The anomeric proton of the rhamnose appeared at δ 5.26 and complex signal at δ 1.32 showed methyl group of rhamnose. Mass spectrum of SA-IV showed [M^+] peak at *m/z* 448 and the loss of a rhamnose moiety from the molecular ion gave a fragment ion peak at *m/z* 302.

On the basis of above deliberations, structure to the compound SA-IV was assigned as; Quercetin-3-O-α-L-rhamnopyranoside.

OH OH HO O CH3 O H H O O H OH OH OH O H OH H

SA-IV

Thanks are due to the Head, Regional Sophisticated Instrumentation Centre, CDRI, Lucknow for recording various spectra and Head, Department of Chemistry, Dr. H.S. Gour University for providing facilities.

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3. Subject/Sub-disciplines of your expertise in which you are willing to act as Referee.

Sl. No.	Major Disciplines (Such as Physics etc.)	Sub-discipline alonwith super-speciality	Experimental/Theoretical or both
1.		(i) (a) (b)	
2.		(ii) (a) (b)	
3.		(iii) (a) (b)	

(II) Suggestions regarding additional referees

Sl. No.	Name(s) & Address of those whom you suggest for refereeing	His/Her Major Disciplines (such as Physics etc.)	His/Her Sub-disciplines alongwith any Super-specialities	Experimental/Theoretical or Both
1.			(i) (a) (b)	
2.			(i) (a) (b)	
3.			(i) (a) (b)	

Signature of the Fellow/Member

THE NATIONAL ACADEMY OF SCIENCES, INDIA

5, Lajpatrai Road, New Katra, Allahabad - 211002

Guidelines for the Authors/Contributors for submitting papers

Proceedings of the National Academy of Sciences, India
(Section A – Physical Sciences)

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The following categories of papers are published in the Proceedings of the National Academy of Sciences, India (Section A Physical Sciences) ·

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[B) WHO CAN SUBMIT

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However, if the Editorial Board finds it necessary, it may get the paper reviewed again.

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The authors may submit the papers directly or forwarded through a Fellow of the Academy as prescribed above. It is mandatory to submit "An Electronic Version" as well as "three hard-copies". The text of the manuscript as per format of the journal outlined below, and preferably with scanned figures, should be supplied as a plain ASCII file (Wordstar 5.5 or 7.0 and Microsoft Word for Window 6.0 are also acceptable, but ASCII is preferred). The language of the journal is English.

[E] FORMAT OF THE MANUSCRIPT

(i) Title of the paper should be in **bold** and running (14-font size) through the full page width.

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(iii) **Abstract** should be typed in 8 point font sizes **"bold"**

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(a) This is to be typed on A4 page in double space in10 point font size.

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(c) Please note that the Proceedings are published in "two column format". Therefore, the authors are required to draw the figures tables/equations in such a way that they can be easily reduced to one column width (~ 7.5 cm) at the time of publication. Figures must be original drawings or exceptionally sharp glossy prints drawn with stencil and UNO pen.

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1. Mirri, M.A. (1982), J. Chem. Phys. 58: 282 (for articles in journals)

White, M. J. D. (1973) Animal Cytology and Evolution, 3rd Ed., Cambridge University Press, London, p. 320 (for books)

Osgood, C.F. (1977) in Number Theory and Algebra: ed., Zasserhause, H., Academic Press, New York, p. 10 (for edited books)

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